VOLUME 29 SECOND SERIES NUMBER 2

THE PHYSICAL REVIEW

A JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS

PUBLISHED BY THE

AMERICAN PHYSICAL SOCIETY

Editorial Service

Managing Editor, [illegible] Tate, University of Minnesota, Minneapolis
E. Darrow, E. C. Kemble, F. L. Mohler, J. A. Gray, C. E. M. Jansen,
J. H. Van Vleck, [illegible] W. Bridgman, [illegible]

FEBRUARY, 1927

[illegible] of Magnesium [illegible] — Bowen, M. Millikan and P. D. Hamblen 233
[illegible] of Boron, Carbon, [illegible] Oxygen and Fluorine — L. M. Mott 251
[illegible] of Electrons — [illegible] 266
[illegible] on a Rotating [illegible] — [illegible] and Warren P. Mason 346
[illegible] — [illegible] E. Ives and C. H. Ives Wall 355
[illegible] in the Ultra-[illegible] — E. [illegible] and J. T. Hall 369
Coated Cells — [illegible] Hunsaker 379
[illegible] of Hydrogen [illegible] — Louis Foster 385
[illegible] Index of [illegible] — E. W. Comer 396
[illegible] of Gas [illegible] by [illegible] — A. P. Carman and K. H. Howard 409
[illegible] of the Hydrogen [illegible] — T. R. Hogness and J. A. Taylor 417
[illegible] of Evaporation [illegible] — E. L. Kinsella 421
[illegible] with [illegible] — C. W. Hewlett 429
[illegible] Distributing Alternating [illegible] — V. Bush and Kent E. Gould 437
[illegible] 445

PROCEEDINGS OF THE AMERICAN PHYSICAL SOCIETY
[illegible] December 1-27—Abstracts of Papers 449

PUBLISHED BY THE AMERICAN PHYSICAL SOCIETY

Second Series *February, 1927* *Vol. 29, No. 2*

THE

PHYSICAL REVIEW

THE CRYSTAL STRUCTURE OF MAGNESIUM PLATINOCYANIDE HEPTAHYDRATE

By Richard M. Bozorth and F. E. Haworth

Abstract

Positions of the Mg and Pt atoms in crystals of $MgPt(CN)_4 \cdot 7H_2O$. These have been definitely determined by means of x-ray oscillating-crystal photographs and Laue photographs, using the theory of space-groups. Because the other atoms are too light in comparison with the metal atoms, especially Pt, their positions could not be determined. The Pt atoms are located at 0 0 0 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, the Mg atoms at 0 0 $\frac{1}{2}$ and $\frac{1}{2}\frac{1}{2}$ 0, in a tetragonal unit of structure 14.6A×14.6A×3.13A. Two units of structure are shown in the figure. The peculiar *optical properties* are believed to be associated with the unusual arrangement of the heavier atoms in widely spaced rows parallel to the tetragonal axis. In these rows Mg atoms alternate with Pt atoms, and the distance between any two adjacent atom-centers is 1.57A. The shortest distance between rows, however, is 10.3A, 6.6 times the distance between atoms in the same row. The *atomic radii* of Mg and Pt as determined by Bragg from other crystal data do not agree with the observed distance between these atoms, the calculated value being 2.7A, the observed distance 1.57A. The observed distance, however, is consistent with that calculated by the method of Davey, who assumes that the radius of an ionized atom differs much from the radius of the same atom un-ionized, and that the radii of Cs^+ and I^- are substantially equal in crystals of CsI.

Introduction

TETRAGONAL crystals of $MgPt(CN)_4 \cdot 7H_2O$[1] are of special interest because of their peculiar optical properties[2] and resultant beautiful appearance. They are red by transmitted light, but by reflected light the prism faces are a brilliant metallic green and the ends of the prism, perpendicular to the tetragonal axis, have a violet

[1] The water content is said to vary *continuously* from 8.1 H_2O to 6.8 H_2O, when exposed to dry air, the crystals being similar in this respect to the zeolites. See H. B. Buxhoevden and G. Tammann, Zeit. anorg. Chem., **15**, 319–327 (1897); and J. W. Mellor, Comprehensive Treatise of Inorganic and Theoretical Chemistry, Longmans Green and Co., **6**, 575–576 (1925).

[2] R. W. Wood, Physical Optics, 2nd Ed., The Macmillan Co., New York, 560–561 (1919). For a bibliography of this and other platinocyanides, and their crystallography, see Gmelin-Kraut, Handbuch der Chemie, Carl Winter, Heidelberg, 5 .3, 867–868 (1915).

tinge. They exhibit strong dichroic fluorescence; rays polarized in the direction of the tetragonal axis are yellow, those polarized perpendicular to the axis are red. Other hydrated salts containing the platinocyanide ion fluoresce when exposed to ultra-violet light or radium, but with these salts the fluorescence does not appear to be polarized as it is in the magnesium salt. None of these other salts is known to be tetragonal, being either orthorhombic or monoclinic.

The crystals have been examined crystallographically by Lang,[3] who observed the forms $\{100\}$, $\{001\}$ and $\{111\}$, and found the axial ratio $c/a=0.6103$.

The determination of the crystal structure was undertaken at the suggestion of H. E. Ives of these laboratories, in the hope that it might furnish some suggestion for an explanation of the optical behavior. The crystals were prepared by slow evaporation of an aqueous solution. X-ray data were obtained from oscillating-crystal photographs and Laue photographs.

The Unit of Structure

Molybdenum K-radiation was reflected onto a photographic plate from $(100)'$ and $(001)'$ faces (primed crystallographic indices are those according to Lang[3]) of an oscillating crystal, using a calcite crystal for comparison. The sines of the grazing angles θ for reflection are given in Table I. The wave-length of the $K\alpha_1$ line is taken to be 0.7075A, and the grating space of calcite 3.029A.[4]

TABLE I

Oscillating-crystal data, using Mo $K\alpha_1$ radiation, $\lambda=0.7075A$

(*hkl*) Old	New	sin θ	(*hkl*) Old	New	sin θ
$(100)'$	(110)	0.034	$(001)'$	(001)	0.226
		0.0686			
		0.1028			
		0.1369			
		0.1711			
		0.2054			

If that reflection from each face which occurs at the smallest angle is considered to be in the first order, the dimensions of the corresponding unit of structure are $10.3A\times10.3A\times1.57A$. However, when the content of this unit is calculated from the density, directly measured as 2.39 g/cm^3, it is found to be only 1/2 molecule of $MgPt(CN)_4\cdot 7H_2O$.

[3] V.v. Lang. Sitz. Ber. Akad. Wiss. Wien, **111** .2a, 1161 (1902).

[4] A. H. Compton, H. N. Beets and O. K. De Foe, Phys. Rev. (2) **25**, 625–629 (1925).

Analysis of Laue photographs (tungsten target x-ray tube) taken with the beam perpendicular to the (001)′ face and perpendicular to the (100)′ face showed that the unit of structure must be enlarged to 14.6A×14.6A×3.13A, containing two molecules. The faces originally designated (100)′, (001)′ and (111)′ by the crystallographers now become (110), (001) and (041), respectively. Hereafter, all indices will be referred to the new unit just described, containing two molecules.

In analyzing the Laue photographs, spots were projected onto a gnomonic net, and the wave-lengths calculated according to the equation

$$n\lambda = 2d_{100}(h^2 + k^2 + l^2a^2/c^2)^{-1/2} \sin\theta$$

where λ is the wave-length of the x-rays, $d_{100} = 14.6$A, $c/a = d_{001}/d_{100}$, $d_{001} = 3.13$A, and h, k and l are the indices of the reflecting plane. The smallest value of $n\lambda$ calculated for any spot was found to be 0.25A, a value consistent with the voltage across the tube, therefore reflections for which the value of $n\lambda$ lay between 0.25 and 0.50A were considered to be first order reflections only. For all planes which reflected in the first order, $h+k+l$ was an even number, consequently the structure is built on a body-centered lattice. Planes for which $h+k+l$ was odd were considered to reflect only in the second order when $n\lambda$ lay between 0.50 and 1.00A.

The Space-Group and the Arrangement of the Atoms

All types of forms, that is, forms whose indices represented all com binations of odd and even indices (including forms $\{001\}$, $\{0kl\}$, $\{hk0\}$, $\{h \cdot h \cdot 2p+1\}$ and $\{h \cdot h \cdot 4p\}$, where p is any integer) reflected in either the first or second order depending *only* on whether $h+k+l$ was an even or an odd number. Furthermore, the Laue photograph taken with the x-ray beam perpendicular to the (001) planes showed a tetragonal axis of symmetry and four reflection planes; and the photograph for which the beam was perpendicular to the (110) planes showed a digonal axis of symmetry and two reflecting planes. The only space-groups[5] with which these data are consistent are D_{4h}^{17}, D_{4}^{9}, C_{4v}^{9} and $D_{2d}^{11} = V_d^{11}$. Since there is no evidence that the crystals do not possess all the symmetry which it is possible for a tetragonal crystal to possess, the correct space-group is probably D_{4h}^{17}.

[5] W. T. Astbury and Kathleen Yardley, Phil. Trans. Roy. Soc. Lond., **224A** 221–257 (1924).

The arrangements[6] predicted by all of these space-groups except C_{4v}^9 for two equivalent atoms in a unit of structure, are the same, namely:

$$(1)\ 0\,0\,0,\ \tfrac{1}{2}\,\tfrac{1}{2}\,\tfrac{1}{2} \qquad (2)\ 0\,0\,\tfrac{1}{2},\ \tfrac{1}{2}\,\tfrac{1}{2}\,0.$$

The atom-positions predicted by C_{4v}^9 are:

$$(3)\ 0\,0\,u\ ;\ \tfrac{1}{2},\ \tfrac{1}{2},\ \tfrac{1}{2}+u\ ;$$

where u may have values between zero and unity. In either case the Mg and Pt atoms are placed in lines parallel to the tetragonal axis, and each line is composed of both kinds of atoms arranged alternately. If the values of u are put equal to 0 and $\frac{1}{2}$, the positions of the atoms according to (3) are those specified in (1) and (2). Although the x-ray diffraction data do not rule out arrangement (3) for values of u which do not differ by $\frac{1}{2}$, physical considerations make it very probable that the atoms lie in the unique positions. If they were not so placed these atoms would be grouped in pairs, each Mg atom, for example, being nearer to one of its neighboring Pt atoms than to any other Pt atom, and the shortest distance between the centers of a Mg and a Pt atom would be less than 1.57A, a distance already considerably smaller than that to be expected on the basis of Bragg's values of atomic radii,[7] or of Wyckoff's more recent tabulation,[8] although not surprisingly small according to Davey's hypothesis.[9]

The x-ray data are of course quite powerless to place the C, N, O or H atoms, since the reflecting powers of these atoms are much less than those of the Mg and Pt atoms. Possible arrangements for C and N atoms include those placing them at the corners of squares of undetermined sizes which lie in planes parallel to (001) planes and which have Pt atoms at their centers. Such an arrangement is similar to that of the Cl atoms around the Pt atoms in K_2PtCl_4.[10]

Seven molecules of H_2O cannot be placed in a manner consistent with the apparent high symmetry. It is suggested as probable that the

[6] R. W. G. Wyckoff, The Analytical Expression of the Results of the Theory of Space-Groups, Carnegie Institution of Washington Publication No. 318, 78–99 (1922).

[7] W. L. Bragg, Phil. Mag. (6) **40**, 169–189 (1920). The radius assigned to Mg is 1.42A. The radius of Pt is not given in this article but may be calculated from more recent data [Pt to Cl, 2.33A in K_2PtCl_4, R. G. Dickinson, J. Am. Chem. Soc. **44**, 2409 (1922)] using Bragg's radius for Cl, 1.05A. This gives for Pt the radius 1.28A. The distance Mg–Pt from these data is 2.7A, a value to be compared with 1.6A, the distance Mg–Pt here found by experiment in $MgPt(CN)_4 \cdot 7H_2O$.

[8] R. W. G. Wyckoff, Proc. Nat. Acad. Sci., **9**, 33–38 (1923).

[9] W. P. Davey, Gen. Elect. Rev., **29**, 274–287 (1926).

[10] R. G. Dickinson, loc. cit. 7.

highest observed water content,[1] corresponding to $MgPt(CN)_4 \cdot 8H_2O$, is that characteristic of perfect crystals. The 16 oxygen atoms, and also the 32 hydrogen atoms, can then be placed in equivalent positions according to arrangements derived from the space-group D_{4h}^{17}, the only one of the possible space-groups listed above which will permit 32 atoms to be arranged in equivalent positions.

Data from one of the Laue photographs are given in Table II, where d/n and λ are expressed in A, and I is the estimated photographic

TABLE II

Laue photographic data for $MgPt(CN)_4 \cdot 7H_2O$. *W radiation incident normally upon (110) planes*

$n^*(hkl)$	d/n	I	λ	$n(hkl)$	d/n	I	λ
(3̄41)	2.13A	5	0.44A	(7̄.12.1)	0.99A	0.4	0.47A
(4̄51)	1.83	2	.33	(053)	.99	.5	.47
(5̄61)	1.60	0.3	.25	2(3̄51)	.97	.3	.37
(112)	1.56	4	.46	(1̄63)	.96	.5	.45
(1̄32)	1.49	3	.42	(2̄73)	.93	.4	.42
2(3̄40)	1.45	1	.42	(8̄.13.1)	.91	.3	.40
(3̄52)	1.33	0.7	.34	(7̄.11.2)	.91	.2	.32
(7̄90)	1.27	.6	.32	2(4̄70)	.90	.2	.47
(6̄91)	1.23	.8	.44	(3̄83)	.89	.3	.38
(5̄72)	1.15	.1	.25	(4̄93)	.85	.2	.35
2(4̄50)	1.13	.1	.25	2(4̄61)	.85	.1	.28
2(2̄41)	1.13	.3	.49	(9̄.14.1)	.84	.2	.34
(7̄.11.0)	1.11	.4	.48	(7̄.13.2)	.83	.3	.40
(7̄.10.1)	1.11	.4	.36	(334)	.77	.1	.34
(5̄92)	1.05	.5	.42	(3̄54)	.75	.1	.44
(123)	1.04	.3	.31	(1̄74)	.73	.1	.42
(233)	1.01	.3	.50	(15.9.2)	.73	.05	.32
(8̄.11.1)	1.01	.3	.30	(1̄94)	.71	.1	.39
(143)	1.00	.3	.50	(3̄.11.4)	.67	.1	.35

* $n=1$ unless otherwise stated.

intensity of the spot. In this table are included all planes having $d/n > 1.00$A which were inclined to the x-ray beam so that they could have reflected any wave-lengths between 0.25 and 0.50A.

DISCUSSION OF THE RESULTS

(a) *Optical properties.* As mentioned in the introduction, the fluorescent light is different in character depending on whether the plane of the analyzer is set parallel to or perpendicular to the tetragonal axis. Although some such difference would be expected for any fluorescent tetragonal crystal, a difference as large as that found for $MgPt(CN)_4 \cdot 7H_2O$ is not ordinarily observed. The reason for the peculiar optical properties of this crystal appear to be closely associated with the relative positions of the Mg and Pt atoms in it. These

atoms are arranged in rows parallel to the tetragonal axis, the distance between atom-centers in any one row being 1.57A. The shortest distance between any two rows, however, is 10.3A, 6.6 times the distance between two atom-centers in the same row. This arrangement is illustrated, to scale, in Fig. 1. Vibrations of the metal atoms must therefore encounter much greater resistances in the axial direction than in directions perpendicular thereto. Even in the regions between the rows of Mg and Pt atoms where the fluorescent light may possibly originate, the components of the electric field parallel and perpendicular to the axis may be expected to differ greatly in magnitude, producing much different effects upon light polarized in these directions.

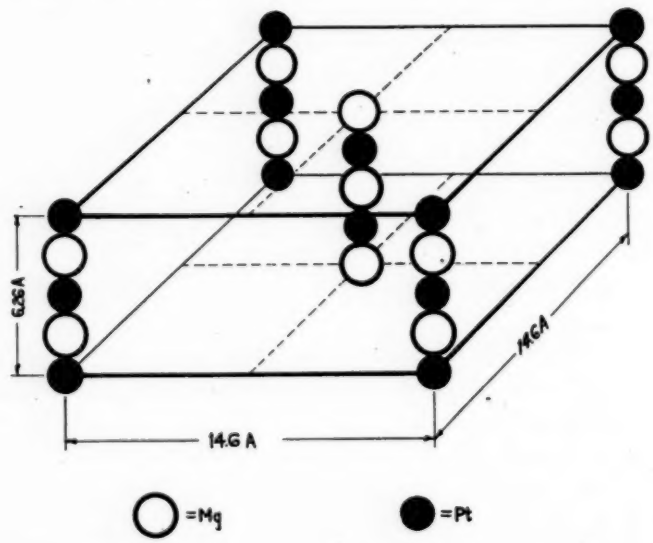

Fig. 1. Arrangement of magnesium platinum atoms in platinocyanide heptahydrate.

(b) *Atomic radii.* Since the original table of atomic radii in crystals proposed by Bragg[7] and based upon the inter-atomic distances observed in FeS_2, Fe, $CaCO_3$, C (diamond), etc., other values have been suggested, based on different methods of allotting to each atom its proper fraction of the total distance between its center and that of its neighbor, the quantity directly determined by means of x-rays. Wyckoff[8] has used the distances in $CsCl_2I$ as a starting point, while Davey has assumed that the radii of Cs^+ and I^- are equal in CsI, and has argued that ionized and un-ionized atoms have very different radii. Although it is to be expected that the radius of an atom will depend both upon the kind and upon the arrangement of the surround-

ing atoms, it nevertheless appears that when an atom has a fixed charge it behaves as if it had a "sphere of influence" which does not vary more than 10 percent if the surrounding atoms are not too different in the crystals compared. The radii proposed by Bragg and by Davey, however, differ from each other by much more than this amount, their values for the radius of the Cl^- ion being 1.05 and 1.59 A, and for the K^+ ion 2.07 and 1.55A, respectively. The nature of this difference causes great discrepancies in the predicted distances between ions of like sign such as I^- to I^-, or Mg^{++} to Pt^{++}. Bragg's predicted distance between I^- ions is 2.80A, while the observed distance is 4.21A in CdI_2 [11] and in SnI_4.[12] The predicted distance between S^{--} ions in MoS_2 [13] is 2.05A, the observed distance 3.49A.

It may be argued that the radii of negative ions "in contact" with each other will be greater than their radii in contact with positive ions, for the similar charges might be expected to keep them farther apart. This same argument, however, would tend to increase the distance between Mg^{++} and Pt^{++} ions to a value much greater than 2.70A, the sum of the Bragg radii, while the distance here observed is only 1.57A. All these discrepancies noted above may be removed by assigning to Mg^{++} a radius 0.87A, consistent with Davey's ideas, and to Pt^{++} a radius 0.70A, consistent with the distance between Pt^{++} and Cl^- in K_2PtCl_4 [10] and with Davey's value for the radius of the Cl^- ion. The structure of $MgPt(CN)_4 \cdot 7H_2O$ accordingly lends support to Davey's method of calculating atomic radii and to the results already obtained by this method.

Since writing the above, the authors have read the paper by W. L. Bragg on "Interatomic Distances in Crystals,"[14] in which he states that the radii given in his 1920 paper should be corrected by about 0.7A, the radii of the anions being increased and those of the cations decreased by this amount. This brings the radii into agreement with the values proposed by Wasastjerna[15] in 1923, but they still differ by about 0.2A from those proposed by Davey. A set of values which is intermediate between these two, and therefore not very different from either of them, may be obtained from the four relations:

$Mg^{++}+Pt^{++}=1.57$ (obs. in $MgPt(CN)_4 \cdot 7H_2O$), $Pt^{++}+Cl^-=2.33$

[11] R. M. Bozorth, J. Am. Chem. Soc., **44**, 2232–2236 (1922).
[12] R. G. Dickinson, J. Am. Chem. Soc., **45**, 958–962 (1923).
[13] R. G. Dickinson and L. Pauling, J. Am. Chem. Soc. **45**, 1466–1471 (1923).
[14] W. L. Bragg, Phil. Mag. (7) **2**, 258–266 (1926).
[15] J. A. Wasastjerna, Soc. Sci. Fennica Comm. Phys.-Nat. **1**, No. 38, 1–25 (1923).

(obs. in K_2PtCl_4)[10], $Mg^{++}+O^{--}=2.10$ (obs. in MgO),[16] and $Cl^{-}-O^{--}=0.40$ (commonly accepted difference). Values so obtained are given in Table III.

TABLE III

Ion	Bragg (1920)	Wasastjerna (1923) Bragg (1926)	Davey (1926)	Calculated
Cl^{-}	1.05A	1.72A	1.59A	1.63A
O^{--}	0.65	1.32	>1.05	1.23
Mg^{++}	1.42	0.75	<1.05	0.87
Pt^{++}	(1.28)	——	——	0.70

Both Wasastjerna's values, and Davey's values as far as they go, are consistent with the observed distance between Mg^{++} and Pt^{++} in $MgPt(CN)_4 \cdot 7H_2O$, and the agreement with each seems good considering that the radius of the "sphere of influence" may be expected to change with the kind and arrangement of the surrounding atoms, and indeed the "radius" may be different in different directions especially in the case of atoms surrounded as are the Mg^{++} and Pt^{++} in $MgPt(CN)_4 \cdot 7H_2O$.

BELL TELEPHONE LABORATORIES, INC.,
September 15, 1926.

$s^2 p^3 = a$ $\quad s^2 p^{3-1} ns = nK$

$s\, p^{3+1} = b$ $\quad s^2 p^{3-1} np = n$

$p^{3+2} = c$ $\quad s^2 p^{3-1} nd = n$

[16] R. W. G. Wyckoff, Am. J. Sci. 10, 107 (1925).

SERIES SPECTRA OF BORON, CARBON, NITROGEN, OXYGEN, AND FLUORINE

By I. S. Bowen

Abstract

Practically all of the unidentified strong lines of boron, carbon, nitrogen, oxygen, and fluorine occurring in the extreme ultra-violet spectra of the vacuum spark have been classified as due to jumps between levels in B_I, C_I, C_{II}, N_{II}, N_{III}, O_{II}, O_{III}, O_{IV}, F_I, F_{II}, F_{III}, and F_{IV}. The levels thus found are correlated with those demanded by the Russell-Heisenberg-Pauli-Hund theory.

I. Introduction

In previous articles by Professor Millikan and the author[1] the series spectra of one and two-valence-electron atoms of the elements in the first row of the periodic table have been traced. The present paper is an extension of the methods there used to the more complex atoms of this same group of elements.

Since the spectra of these elements are much more complex than those previously studied and as the Russell-Heisenberg-Pauli-Hund theory has shown, there is, in general, no direct connection between the type of the term, i. e. S, P, D, F, and the corresponding k value of the electrons involved, a further extension of the notation is necessary. The notation used throughout this paper is as follows: All terms arising from the normal state of the atom of any n electron system, i. e. that due to the configuration of 2 s electrons and $(n-2)$ p electrons or in Russell's notation the s^2p^{n-2} configuration, are designated by a. Those terms due to the configuration formed when one of the s electrons is moved to a 2 $p$orbit, i. e. the sp^{n-1} configuration are designated by b, while terms which have their origin in the p^n configuration, i. e. the arrangement attained when both of the s electrons are raised to $2p$ orbits, are indicated by c. When one of the p electrons is moved to an excited s orbit making an $s^2p^{n-3} \cdot s$ configuration, the terms thus formed are marked with k preceded by a numeral indicating the total quantum number of the orbit occupied by the excited electron. Likewise, when one of the p electrons is raised to an excited p or d orbit forming an $s^2p^{n-3} \cdot p$ or an $s^2p^{n-3} \cdot d$ configuration, the terms produced are designated by m and n respectively.

[1] Bowen and Millikan, Proc. Nat. Acad. Sci. **10**, 199 (1924).
Bowen and Millikan, Phys. Rev. **26**, 310 (1925); **28**, 256 (1926).

The maximum term multiplicity is indicated in the usual way by a small figure written above and at the left of the letter indicating the type of the term. In the tables where no ambiguity can arise as to

TABLE I

Series lines of B_I

Int.	λ I. A. Vac.	ν	Δν	Designation	Term Values	
1	1825.89	54767.8	15.9	aP_1-3nD	aP_1	67544.6
2	1826.42	54751.9		aP_2-3nD	aP_2	67529.1
3	2089.59	47856.3	15.1	aP_1-bD	bD	19688.1
3	2090.25	47841.2		aP_2-bD		
	2497.53	40039.6	15.3	aP_1-3kS	$3kS$	27504.9
	2498.48	40024.3		aP_2-3kS	$3nD$	12777.0

the multiplicity of the term, the indices are omitted. In the present notation primes are omitted as no longer necessary.

II. THREE-ELECTRON SYSTEMS

Since in atoms of this type one electron only is in an uncompleted group, the Hund theory predicts that the type of any term is the same as that of the orbit in which the excited electron finds itself, i. e. when the electron is in an s orbit it gives rise to a ^2S term, when in a p orbit to a ^2P term, etc. All of these terms belong to the doublet system. This, of course, is true only so long as the p electron alone is excited and the completed group of $2s$ electrons is left undisturbed. Jumps between terms thus formed by the excitation of the single p electron result in the regular doublet series of lines in these atoms. In C_{II} these series have been very completely analyzed by Fowler.[2] Table II includes only those of Fowler's lines for which much greater accuracy and resolution can now be obtained than were available at the time his article was written. For this reason the present table of C_{II} lines should be considered as supplementary to his. In the case of N_{III} Fowler[3] has also identified the first term of the principal and of the second diffuse series, but was unable to obtain the lines corresponding to jumps of the electron to its normal position in the atom. The position of these resonance lines can be predicted with a considerable degree of accuracy by extrapolation from the corresponding

[2] A. Fowler, Proc. Roy. Soc. 105, 299 (1924).
[3] A. Fowler, Series in Line Spectra, p. 165.

TABLE II

Series lines of C_{II}

Int.	λ I. A. Vac.	ν	Δν	Designation	Term Values	
		Doublets				
2	594.79	168127.	65.	aP_1-4nD	aP_1	196658.8
2	595.02	168062.		aP_2-4nD	aP_2	196595.0
5	687.053	145549.2	63.1	aP_1-3nD	bS	100164.9
5	687.351	145486.1		aP_2-3nD	bP_1	86033.9
					bP_2	85992.3
5	858.088	116538.2	64.2	aP_1-3kS	bD	121727.4
6	858.561	116474.0		aP_2-3kS		
7	903.620	110666.0		aP_1-bP_2		
8	903.960	110624.4	62.8	aP_1-bP_1		
8	904.133	110603.2	62.7	aP_2-bP_2		
7	904.472	110561.7		aP_2-bP_1		
6	1036.336	96493.8	63.7	aP_1-bS		
6	1037.021	96430.1		aP_2-bS		
2	1141.61	87595.6		$bD-4mP$		
10	1334.539	74932.2	65.4	aP_1-bD		
10	1335.705	74866.8		aP_2-bD		
2	1760.44	56804.0	13.2	$bD-3mP_2$		
1	1760.85	56790.8		$bD-3mP_1$		
		Quartets				
5	1009.870	99022.6	21.5	$^4bP_1-cS$		
6	1010.090	99001.1	28.6	$^4bP_2-cS$		
6	1010.382	98972.5		$^4bP_3-cS$		

lines of B_I and C_{II} using the method already applied to the identification of similar lines in C_{III}.[1] This method leads to the identification of the 452A and the 374A lines as given in Table III. Since the 374A line falls very close to a strong oxygen line, its wave-length may be somewhat in error.

The Hund theory further predicts that when one of the s electrons is removed to a $2p$ orbit the sp^2 configuration thus formed will give rise to a quartet ^4P term and doublet ^2S, ^2P and ^2D terms. If the second s electron is moved to a $2p$ position making a p^3 configuration,

then ^4S, ^2P and ^2D terms will result. All of the doublet terms due to the sp^2 configuration should combine strongly with the normal doublet a^2p level of the s^2p configuration. Since all of the electrons in both

TABLE III

Series lines of N_{III}

Int.	λ I. A. Vac.	ν	Δν	Designation	Term Values	
	Doublets					
1	374.31	267158.		$aP-3nD$	aP_1	382225.8
					aP_2	382051.4
1	451.91	221283.	161.	aP_1-3kS		
1	452.24	221122.		aP_2-3kS	bS	251223.4
5	684.997	145986.0		aP_1-bP_2	bP_1	236351.0
6	685.519	145874.9	175.1	aP_1-bP_1	bP_2	236240.2
6	685.820	145810.9	174.5	aP_2-bP_2	bD_2	281195.6
5	686.340	145700.4		aP_2-bP_1	bD_3	281201.3
					cP	151222.1
5	763.348	131001.8	173.1	aP_1-bS		
5	764.358	130828.7		aP_2-bS	$3kS$	160936.1
2	772.903	129382.3	12.8	bD_3-cP		
2	772.980	129369.5		bD_2-cP	$3mP_1$	136572.85
					$3mP_2$	136536.82
7	989.803	101030.2	180.1	aP_1-bD		
7	991.571	100850.1		aP_2-bD	$3nD_2$	115000.
					$3nD_3$	114994.14
1	1006.03	99400.6		$bS-cP$		
3	1183.04	84528.2	108.0	bP_1-cP		
3	1184.55	84420.2		bP_2-cP		
	4098.48	24399.30	36.08	$3kS-3mP_2$		
	4104.55	24363.22		$3kS-3mP_1$		
	4635.46	21572.83	35.99	$3mP_1-3nD_2$		
	4641.94	21542.70	5.86	$3mP_2-3nD_3$		
	4643.21	21536.84		$3mP_2-3nD_2$		
	Quartets					
3	771.545	129610.1	60.3	bP_1-cS		
4	771.904	129549.8	80.5	bP_2-cS		
4	772.384	129469.3		bP_3-cS		

arrangements are in 2-total-quantum-number orbits, all lines due to combinations between them should obey the irregular doublet law.

In carbon, nitrogen, and oxygen[4] Professor Millikan and the author have already identified a pp' group fulfilling these conditions. This group is evidently the combination between the a^2P and the b^2P levels. In C_{II} Fowler has found an x level which combines strongly with the low a^2P level to produce the strong lines at 1036A. This is unquestionably the b^2S term of the sp^2 configuration, since the lines connecting it with the ^2P levels have, within experimental error, exactly the separation of the ^2P levels. The strongest lines in the carbon spectrum are a pair at 1335A, which is shown by the data in the present paper, and also by some of Lang and Smith's data,[5] to have a separation about 2 frequency units larger than that of the true a^2P separation as obtained from the a^2P-b^2P group at 904A. These lines are definitely due to C_{II}, for if we assume them to be due to a jump into the a^2P level then the levels from which this jump starts combining with the $3m^2P$ and the $4m^2P$ levels would give rise to lines at 1760A and 1141A. These lines are observed at almost exactly their calculated position, and the 1760A doublet which is the only one that can be resolved shows a separation about 2 frequency units larger than that of the $3m^2P$ levels involved. These considerations make it practically certain that this unidentified level is the b^2D term of the sp^2 configuration. Since all combinations with ^2P terms show separations slightly larger than that of the ^2P terms themselves it is evident that these b^2D terms are inverted.

TABLE IV

Irregular doublets, three-electron systems

Element	ν	$\Delta\nu$	ν	$\Delta\nu$
	aP_2-bS		aP_2-bP_1	
C_{II}	96430.1		110561.7	
		34398.6		35138.7
N_{III}	130828.7		145700.4	
		33152.3		34392.6
O_{IV}	163981.		180093.	
	aP_2-bD		bP_2-cS	
B_I	47841.2			
		27025.6		
C_{II}	74866.8		98972.5	
		25983.3		30496.8
N_{III}	100850.1		129469.3	
		25699.3		30313.7
O_{IV}	126549.4		159783.	

[4] Bowen and Millikan, Phys. Rev. **26**, 150 (1925).
[5] Lang and Smith, J.O.S.A. & R.S.I. **12**, 523 (1926).

The line due to the change from these b^2S and b^2P levels to the a^2P levels can be traced from C_{II} to O_{IV} while those due to the jump from b^2D to a^2P can be traced from B_I to O_{IV}. In each case, where accuracy of measurement is sufficient to detect it, this last pair shows a separation slightly larger than that of the other two. In all cases the lines due to these jumps follow the irregular doublet law as shown in Table IV.

That lines involving the b^2S and b^2P levels are missing in B_I, or at least are so weak that they cannot be obtained in high enough orders to be resolved, is probably due to the fact that these levels have negative term values, i. e. it requires more energy to produce these levels than it does to ionize the atom by removing the p electron.

In N_{III} and O_{IV} additional lines are observed which are obviously due to the combination between the b^2S, b^2P, and b^2D terms and the c^2P term of the p^3 configuration. That these lines are missing or very weak in C_{II} is probably due to the fact that the c^2P term involves an energy nearly equal to that of ionization of C_{II}.

In addition to the doublet lines already mentioned, we should expect the lines due to the combination between the quartet b^4P and the quartet c^4S term. Such a group of lines following the irregular doublet law (see Table IV) and having the relative separations characteristic of quartets, has been traced from C_{II} to O_{IV}. While no other lines involving the b^4P level can be located to check this identification, yet it seems certain since the variation of intensity of the lines in going from element to element is such as to indicate that they belong to a three-electron system. Further there is no place for such lines in the Hund scheme for either the two or four-electron systems.

The term values in C_{II} given in Table II are based on Fowler's value for the $3m^2P$ term, while those given in Tables I and III for B_I and N_{III} are based on that of the $3n^2D$ term which was assumed equal to 1/4 and 9/4 respectively of that of the corresponding term in C_{II}. This method gives results that are probably accurate to 1000 frequency units in B_I and 3000 or 4000 in N_{III}. Since it has not been possible to make any positive identification of the a^2P-$3k^2S$ and a^2P-$3n^2D$ lines in O_{IV} no term values are given in Table V. Methods similar to those used in identifying these lines in N_{III} seem to indicate that a^2P-$3k^2S$ is the 279.7A line[6] and a^2P-$3n^2D$ is the 238.6A line. In any case the lines must fall very close to these positions. If we assume the identification of 238.6A is correct and further assume a value for $3n^2D$ 16/4 times as great as in C_{II} we get $a^2P = 623500$ fre-

[6] Millikan and Bowen, Phys. Rev. **23**, 1 (1924).

TABLE V

Series lines of O IV

Int.	λ I. A. Vac.	ν	Δν	Designation
		Doublets		
4	553.318	180728.		aP_1-bP_2
5	554.066	180484.	388.	aP_1-bP_1
5	554.507	180340.	391.	aP_2-bP_2
4	555.270	180093.		aP_2-bP_1
4	608.390	164368.	387.	aP_1-bS
4	609.828	163981.		aP_2-bS
1	616.93	162093.		$bD-cP$
6	787.716	126949.3	399.9	aP_1-bD
6	790.205	126549.4		aP_2-bD
1	802.21	124656.		$bS-cP$
2	921.27	108546.	240.	bP_1-cP
3	923.31	108306.		bP_2-cP
		Quartets		
3	624.609	160100.	132.	bP_1-cS
4	625.126	159968.	185.	bP_2-cS
4	625.848	159783.		bP_3-cS

quency units which cannot be an error by more than 1 percent regardless of whether the above identifications are correct or not.

III. FOUR-ELECTRON SYSTEMS

The Hund theory predicts that the different configurations of a four-electron system will be characterized by terms as follows:

s^2p^2 — ^1S, ^1D, ^3P

sp^3 — ^1P, ^1D, ^3S, ^3P, ^3D, ^5S

$s^2p \cdot s$ — ^1P, ^3P

$s^2p \cdot p$ — ^1S, ^1P, ^1D, ^3S, ^3P, ^3D

$s^2p \cdot d$ — ^1P, ^1D, ^1F, ^3P, ^3D, ^3F

Fowler[7] has already analyzed many of the lines in the spectra of N II. His triplet terms should be correlated with those of the Hund

[7] A. Fowler, Proc. Roy. Soc. **107**, 31 (1925).

theory as follows: p_1, p_2, p_3, are due to the $s^2p \cdot 3s$ configuration, d_1, d_2, d_3, and p_1', p_2', p_3' to the $s^2p \cdot 3p$ configuration, d_1', d_2', d_3', to the $s^2p \cdot 3d$ configuration, and p_1^2, p_2^2, p_3^2 to the $s^2p \cdot 4s$ configuration.

TABLE VI

Series lines in C I

Int.	λ I. A. Vac.	ν	Δν	Designation
		Triplets		
3	1328.839	75253.7		aP_0-bP
			14.6	
4	1329.100	75238.9		aP_1-bP
			27.6	
4	1329.583	75211.6		aP_2-bP
3	1560.267	64091.6		aP_0-bD
			16.1	
4	1560.660	64075.5		aP_1-bD
			29.6	
5	1561.381	64045.9		aP_2-bD
2	1656.27	60376.6		aP_1-3kP_2
3	1657.01	60349.7		$aP_{0,2}-3kP_{1,2}$
2	1657.37	60336.6		aP_1-3kP_1
2	1657.92	60316.5		aP_1-3kP_0
2	1658.13	60308.9		aP_2-3kP_1

If this correlation is correct, then p_1, p_2, p_3 and p_1^2, p_2^2, p_3^2 are the first two members of a series of corresponding levels. Due to this fact one can obtain an estimate of the term values, with an error not greater than 1000 or 2000 frequency units, by making these two terms fit a Rydberg formula. Such a calculation indicates that Fowler's term values should be increased by 20300 frequency units. That this value is approximately correct is shown by the fact that it gives to his d' term a value just above 50000 which is similar to that of the terms due to the $s^2p^{n-3} \cdot d$ configuration of other singly ionized atoms of this group of elements.

From the triplet separations of Fowler's terms, lines connecting these terms with the normal ^3P levels were identified and the term value of these levels determined as given in Table VII.

In addition to these lines which are produced when a p electron is excited, other very strong lines should be expected when one of the s electrons is displaced to a $2p$ orbit. As before all lines produced by the return of this electron should follow the irregular doublet law. Such groups of lines, all obeying the irregular doublet law, (see Table VIII)

TABLE VII

Series lines of N II

Int.	λ I. A. Vac.	ν	Δν	Designation	Term Values*	
		Triplets				
3	533.53	187431.		$aP_{0,1}-3nD_{1,2}(-d'_{2,3})$	aP_0	239373.3
					aP_1	239324.7
3	533.71	187368.		$aP_2-3nD_{1,2,3}(-d'_{1,2,3})$	aP_2	239241.6
4	644.633	155127.0	48.8	aP_0-bS		
5	644.836	155078.2	82.7	aP_1-bS	bS	84246.3
5	645.180	154995.5		aP_2-bS	bP_0	130150.0
					$bP_{1,2}$	130155.3
2	671.027	149025.3		$aP_1-3kP_2(-p_1)$	$bD_{1,2}$	147121.4
3	671.397	148943.2		$aP_{0,2}-3kP_{1,2}(-p_{2,1})$	bD_3	147135.2
1	671.650	148887.1		$aP_1-3kP_1(-p_2)$		
2	671.780	148858.3		$aP_1-3kP_0(-p_3)$		
2	672.026	148803.8		$aP_2-3kP_1(-p_2)$		
6	915.603	109217.6	42.9	aP_0-bP_1		
6	915.963	109174.7	6.5	aP_1-bP_0		
6	916.018	109168.2	81.0	$aP_1-bP_{1,2}$		
8	916.698	109087.2		$aP_2-bP_{1,2}$		
6	1083.983	92252.4	49.6	aP_0-bD_1		
7	1084.566	92202.8	82.7	$aP_1-bD_{1,2}$		
3	1085.540	92120.1	13.7	$aP_2-bD_{1,2}$		
8	1085.701	92106.4		aP_2-bD_3		
1	1275.06	78427.7		$bD_3-3mP_2(-p'_1)$		
1	1276.18	78358.9		$bD_{1,2}-3mP_1(-p'_2)$		
0	1276.74	78324.5		$bD_{1,2}-3mP_0(-p'_3)$		

*Assuming $3kP_2\ (p_1).=90300$.

have been traced through the four-electron atoms of this row of the periodic system, with characteristics as follows:

a^3P-b^3S. This group appears as three sharp lines with no further structure. It does not appear in C I for the same reason that a^2P-b^2S does not appear in B I.

a^3P-b^3P. The separations of these lines are very similar to those of the preceding ones. The center component is double in two instances where it has been possible to obtain particularly good resolutions.

These separations are such as to indicate that b^3P_1-b^3P_2 is so small that it cannot be resolved while b^3P_0-b^3P_1 can just be separated with the highest resolution.

TABLE VIII

Irregular doublets, four-electron systems

	aP_2-bS		aP_2-bP		aP_2-bD_3	
	ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$
C_I			75211.6		64045.9	
				33875.6		28060.5
N_{II}	154995.5		109087.2		92106.4	
		41785.5		32987.9		27612.8
O_{III}	196781.		142075.1		119719.2	
		40918.		32551.9		27514.8
F_{IV}	237699.		174627.		147234.	

a^3P-b^3D. In this group of lines the long wave-length component is double, the main line having a weak satellite on the short wave-length side. The separation of the extreme components is a little greater than in the preceding groups, thus indicating an inverted D term.

In O_{III} it has been possible to classify a few singlets by means of constant frequency differences occurring between certain lines.

In Table VII none of the lines of N_{II} identified by Fowler have been included. Many of the lines, however, involve levels classified by him. In such cases where his designation differs from the present one, his has been added in parenthesis.

No term values for C_I and O_{III} are given in Tables VI and IX since no sequence of corresponding levels has been found and no certain identification of the a^3P-$3n^3D$ lines can be made. In C_I the a^3P-$3n^3D$ lines should be found at about 1300A. It may be that a partially resolved group at 1277A should be identified as these lines. If this is correct and $3n^3D$ is assumed 1/4 of its value in N_{II} then a^3P has a value of 91300 which, regardless of the correctness of the identification of 1277A, can hardly be an error by more than 5 percent. Similarly the 374.3A and the 305.7A lines[6] in oxygen are probably a^3P-$3k^3P$ and a^3P-$3n^3D$ respectively, which, if $3n^3D$ is 9/4 of its value in N_{II}, would give a value of $a^3P=443900$, which is probably correct to 2 percent.

TABLE IX

Series lines in O III

Int.	λ I. A. Vac.	ν	Δν	Designation
		Singlets		
0	328.34	304562.	22919.	$aD-3nP$
0	355.06	281643.		$aS-3nP$
2	395.52	252832.	22899.	$aD-3kP$
2	434.91	229933.		$aS-3kP$
6	525.79	190190.	22916.	$aD-bP$
4	597.82	167274.		$aS-bP$
		Triplets		
4	507.384	197089.	116.	aP_0-bS
5	507.684	196973.	192.	aP_1-bS
6	508.180	196781.		aP_2-bS
6	702.327	142383.8	99.3	aP_0-bP_1
6	702.817	142284.5	16.3	aP_1-bP_0
6	702.898	142268.2	193.1	$aP_1-bP_{1,2}$
7	703.853	142075.1		$aP_2-bP_{1,2}$
7	832.926	120058.7	117.4	aP_0-bD_1
8	833.741	119941.3	194.3	$aP_1-bD_{1,2}$
3	835.094	119747.0	27.8	$aP_2-bD_{1,2}$
9	835.288	119719.2		aP_2-bD_3

IV. FIVE-ELECTRON SYSTEMS

For atoms of this type the Hund theory predicts that the terms produced by the various electron configurations will be of the following types:

s^2p^3 — ^4S, ^2D, ^2P

sp^4 — ^4P, ^2P, ^2D, ^2S

$s^2p^2 \cdot s$ — ^4P, ^2P, ^2D, ^2S

$s^2p^2 \cdot p$ — ^4S, ^4P, ^4D, ^2S, ^2P, ^2D, ^2P, ^2D, ^2F, $^2{}_1$

$s^2p^2 \cdot d$ — ^4P, ^4D, ^4F, ^2P, ^2D, ^2F, ^2S, ^2P, ^2D, ^2F, ^2G, ^2D

Hopfield[8] and Kiess[9] have classified the lines of N_I while A. Fowler[10] has classified many of the lines of O_{II} in the region between 2000A and 7000A, and R. H. Fowler and Hartree[11] have correlated the levels obtained by A. Fowler with those demanded by the Hund theory.

TABLE X

Series lines of F_{IV}

Int.	λ I. A. Vac.	ν	Δν	Designation
		Triplets		
0	419.95	238124.	425.	$aP_{0,1}-bS$
0	420.70	237699.		aP_2-bS
2	570.63	175245.	224.	aP_0-bP
3	571.36	175021.	394.	aP_1-bP
4	572.65	174627.		aP_2-bP
4	676.06	147916.	243.	aP_0-bD
5	677.17	147673.	439.	aP_1-bD
5	679.19	147234.		aP_2-bD

In A Fowler's list of levels there were no ^4P terms that could be correlated with the ^4P level due to the $s^2p^2 \cdot d$ configuration. For that reason R. H. Fowler and Hartree identified A. Fowler's x_3 term as this level but marked the correlation as doubtful. While this work was in progress, Professor H. N. Russell pointed out a group of strong lines in the violet that evidently were due to jumps from three levels to all of the quartet terms due to the $s^2p^2 \cdot p$ configuration. Since the term values of these new levels are very close to that of the other quartet terms arising from the $s^2p^2 \cdot d$ configuration it is obvious that they should replace x_3 in R. H. Fowler and Hartree's classification. With Professor Russell's permission his lines and the term values calculated from them are included in Table XI. Still another group of lines which represent combinations between a second triple level and the quartets of the $s^2p^2 \cdot p$ configuration has been found in the region near 2000A. The position and separations of these levels make their assignment as the ^4P term of the $s^2p^2 \cdot 5s$ configuration very certain. Since Fowler has already identified the ^4P terms due to the

[8] Hopfield, Phys. Rev. **27**, 801 (1926).
[9] Kiess, J.O.S.A. & R.S.I. **11**, 1 (1925).
[10] A. Fowler, Proc. Roy. Soc. **110**, 476 (1926).
[11] R. H. Fowler and Hartree, Proc. Roy. Soc. **111**, 83 (1926).

TABLE XI

Series lines of O_{II}

Int.	λ I. A. Vac.	ν	Δν	Designation	Term Values	
		Doublets				
0	440.49	227020.		$aD-3nP(-bp'')$	aP	242554.
1	441.93	226280.		$aD-3nD(-cd')$	aD_2	256192.
					aD_3	256208.
0	470.30	212630.		$aP-3nD(-cd')$		
2	481.53	207671.		$aD-3n'D(-bd')$	bP_1	70262.
					bP_2	70430.
2	483.82	206688.		$aD-3n'P(-ap'')$		
					bD	117029.
3	485.48	205982.		$aD-3nF$		
2	515.47	193998.	57.	$aP-3n'D_3(-bd'_3)$		
2	515.62	193941.		$aP-3n'D_2(-bd'_2)$		
3	518.23	192965.		$aP-3n'P(-ap'')$		
3	537.813	185938.	153.	$aD-bP_1$		
4	538.258	185785.		$aD-bP_2$		
3	580.409	172292.	168.	$aP-bP_1$		
4	580.975	172124.		$aP-bP_2$		
2	600.583	166505.		$aP-3kD(-ad')$		
5	616.309	162256.	198.	$aD-3kP_2(-2p_2)$		
5	617.064	162058.		$aD-3kP_1(-2p_1)$		
6	644.159	155241.		$aP-3kS(-as')$		
5	672.913	148608.	185.	$aP-3kP_2(-2p_2)$		
5	673.752	148423.		$aP-3kP_1(-2p_1)$		
7	718.495	139179.8	14.3	aD_3-bD		
7	718.569	139165.5		aD_2-bD		
6	796.665	125523.3		$aP-bD$		
		Quartets			Term Values*	
2	430.06	232526.		$aS-3nP$		
3	539.067	185506.	157.	$aS-3kP_3(-ap_3)$	aS	283366.
2	539.524	185349.	108.	$aS-3kP_2(-ap_2)$	bP_1	163282.8
1	539.837	185241.		$aS-3kP_1(-ap_1)$	bP_2	163364.9
					bP_3	163528.3
8	832.756	120083.2	82.1	$aS-bP_1$		
9	833.326	120001.1	163.4	$aS-bP_2$	$5kP_1$	25665.5
10	834.462	119837.7		$aS-bP_3$	$5kP_2$	25561.3
					$5kP_3$	25395.4

*Assuming $3kP_3(ap_3)=97860$.

TABLE XI (*continued*)

Int.	λ I. A. Air	ν	Δν	Designation	Term Values	
0	1956.78	51087.7		$3mD_3-5kP_3(d_3-)$		
1	1959.70	51011.6		$3mD_2-5kP_2(d_2-)$	$3nP_1$	50756.79
3	1961.60	50962.2		$3mD_4-5kP_3(d_4-)$	$3nP_2$	50823.28
2	1963.20	50920.6		$3mD_3-5kP_3(d_3-)$	$3nP_3$	50896.37
0	1963.61	50910.0		$3mD_2-5kP_1(d_2-)$		
2	2016.60	49572.4		$3mP_2-5kP_3(p'_2-)$		
2	2020.44	49478.0		$3mP_3-5kP_3(p'_3-)$		
1	2021.45	49453.3		$3mP_1-5kP_2(p'_1-)$		
4	2182.72	45799.9		$3mS-5kP_3(s_3-)$		
2	2190.66	45634.0		$3mS-5kP_2(s_2-)$		
2	2195.70	45529.3		$3mS-5kP_1(s_2-)$		
1	3872.45	25816.15		$3mD_2-3nP_1(d_2-)$		
2	3874.10	25805.16		$3mD_1-3nP_2(d_1-)$		
1	3882.45	25749.66		$3mD_2-3nP_2(d_2-)$		
2	3893.53	25677.05		$3mD_2-3nP_3(d_2-)$		
1	3896.30	25658.13		$3mD_3-3nP_2(d_3-)$		
4	3907.45	25584.92		$3mD_3-3nP_3(d_3-)$		
4	4121.48	24256.31		$3mP_1-3nP_1(p'_1-)$		
2	4129.34	24210.14		$3mP_2-3nP_1(p'_2-)$		
6	4132.82	24189.74		$3mP_1-3nP_2(p'_1-)$		
0	4140.74	24143.49		$3mP_2-3nP_2(p'_2-)$		
7	4153.31	24070.42		$3mP_2-3nP_3(p'_2-)$		
3	4156.54	24051.70		$3mP_3-3nP_3(p'_3-)$		
4	4169.23	23978.50		$3mP_3-3nP_3(p'_3-)$		
4	4890.93	20440.31		$3mS-3nP_1(s_2-)$		
5	4906.88	20373.87		$3mS-3nP_2(s_2-)$		
6	4924.60	20300.57		$3mS-3nP_3(s_2-)$		

$s^2p^2 \cdot 4s$ and $s^2p^2 \cdot 3s$ configurations, this gives a series of three consecutive terms from which it is possible to determine term values with an error of not greater than 30 or 40 frequency units. The progression of k^4P_1 terms was used for this purpose since they are based on the most stable state of the O^{++} ion. This calculation showed that all of Fowler's term values of quartet levels should be decreased by 2140 frequency units.

TABLE XII

Irregular doublets, five-electron systems

	$aS-bP_3$	
	ν	$\Delta\nu$
N_I	88169.4	
	88150.8	
	88106.7	
		31731.0
O_{II}	119837.7	
		32059.3
F_{III}	151897.	

The normal terms of both quartet and doublet systems were then obtained through the various combinations with the terms identified by Fowler and by Russell.

As before the lines due to changes from an sp^4 to an s^2p^3 configuration follow the irregular doublet law as seen in Table XII.

TABLE XIII

Series lines of F_{III}

Int.	λ I. A. Vac.	ν	$\Delta\nu$	Designation
		Doublets		
2	429.49	232834.	357.	$aD-bP_1$
4	430.15	232477.		$aD-bP_2$
2	464.25	215401.	384.	$aP-bP_1$
2	465.08	215017.		$aP-bP_2$
7	567.70	176149.		$aD-bD$
4	630.17	158687.		$aP-bD$
		Quartets		
7	656.10	152416.	177.	$aS-bP_1$
8	656.86	152239.	342.	$aS-bP_2$
8	658.34	151897.		$aS-bP_3$

In Table XI none of the lines identified by Fowler have been included, but where lines involve levels classified by him his designation in parenthesis has been placed after the regular designation. All of the wave-lengths of lines above 1900A are taken from unclassified lines in Fowler's table of O_{II}.

TABLE XIV

Series lines of F_{II}

Int.	λ I. A. Vac.	ν	Δν	Designation
		Triplets		
4	546.84	182869.	344.	aP_2-3kS
3	547.87	182525.	150.	aP_1-3kS
2	548.32	182375.		aP_0-3kS
8	605.67	165106.		aP_2-bP_1
7	606.27	164943.		aP_1-bP_0
9	606.81	164796.		aP_2-bP_2
4	606.95	164758.		aP_1-bP_1
7	607.48	164614.		aP_0-bP_1
8	608.06	164457.		aP_1-bP_2

V. Six- and Seven-Electron Systems

Of the six-electron systems of this group the O_I spectra has already been classified by others.[12] In F_{II} only two groups can be classified

TABLE XV

Series lines of F_I

Int.	λ I. A. Vac.	ν	Δν	Designation
		Doublets		
4	806.92	123928.	410.	aP_2-3nx
3	809.60	123518.		aP_1-3nx
5	951.81	105063.		aP_2-3kP_1
7	954.78	104736.	409.	aP_2-3kP_2
6	955.53	104654.	405.	aP_1-3kP_1
5	958.49	104331.		aP_1-3kP_2

[12] A. Fowler, Series in Line Spectra, p. 166.
Hopfield, Astrophys. J. 59, 114 (1924).

with certainty as shown in Table XIV. It is quite likely that the a^3P-$3n^3D$ line can be identified as a rather weak partially resolved group at 472A. If this is correct and $3n^3D$ is assumed to have a value four times as great as in O_I, then a^3P is equal to 261300 with an error not larger than 5 percent.

In F_I only two groups have been identified in this region, while De Bruin[13] has identified a third doublet pp' group in Carragan's data in the red. Since it involves a separation of 325.6 frequency units, doubtless should be identified as $3k^2P$-$3m^2P$. No term values can be determined with great accuracy, but if we assume $3nx$ equal to 13000 we obtain a^2P equal to 136900, a value which is probably correct to 1 or 2 percent.

NORMAN BRIDGE LABORATORY OF PHYSICS,
CALIFORNIA INSTITUTE OF TECHNOLOGY.
November 11, 1926.

[13] De Bruin, K. Akad. Amsterdam Proc. **35**, 751 (1926).

THE VELOCITY DISTRIBUTION OF ELECTRONS ISSUING FROM SMALL HOLES

By Robert H. Dalton and Warren P. Baxter

Abstract

The velocity distribution of a beam of 50-volt electrons issuing from a hole 0.022 cm in diameter in a copper plate 0.02 cm thick has been measured. Seventy percent of the electrons were found to retain approximately their initial velocity. By coating the sides and edges of the hole with lampblack 95% of the electrons were transmitted without appreciable energy loss. Similar results were obtained with grids of 100 mesh copper gauze.

INTRODUCTION.—Preliminary to the construction of a magnetic electron velocity filter, some experiments were undertaken to determine the effect of passage through small holes or fine-mesh gauzes on the velocity distribution of an electron beam. Lehman and Osgood[1] found that with velocities of the primary beam corresponding to from 200 to 1000 volts less than 1% of the electrons passing through a hole 0.19 mm in diameter in a copper plate 0.135 mm thick retain their initial velocity. Since in similar experiments with 50-volt electrons we

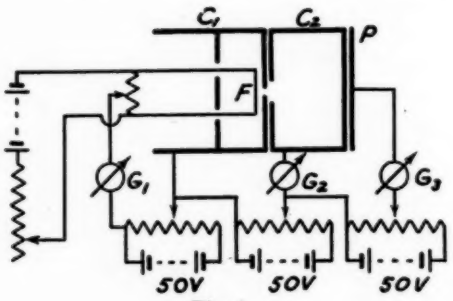

Fig. 1.

were able by using non-reflecting surfaces to get through more than 90% of the electrons with their initial velocity, it seems worth while to publish a brief description of our experiments.

Experimental arrangement. The apparatus is shown diagrammatically in Fig. 1. The source of electrons is a platinum filament F coated with calcium oxide operating on a potential-drop of 2 volts. Surrounding this is the cylindrical copper cage C_1, pierced by a hole 0.022 cm in diameter at a point opposite the center of the filament. The copper in

[1] Lehman and Osgood, Proc. Cambridge Phil. Soc. 22, 731 (1925).

the neighborhood of the hole is 0.02 cm thick, and the distance to the filament is about 0.1 cm. C_2 is a similar cage 2 cm long with a hole 0.5 cm in diameter in the end facing C_1. The ends of the cages are discs which screw into place so that they may readily be replaced by grids, in which case the copper plate P is used to measure the current traversing the second of these. It is about 0.1 cm from C_2. All the cages have an inner diameter of 3 cm. The cages, plate, and filament are mounted rigidly with respect to one another and are suspended with the axis of the cylinders parallel to the earth's magnetic field in a tube closed by a ground-glass stopper (set in sealing wax) and connected with a liquid-air trap, a McLeod gauge, and vacuum pumps. G_1, G_2, and G_3 are galvanometers measuring the total current, the current from C_2, and the plate current, respectively.

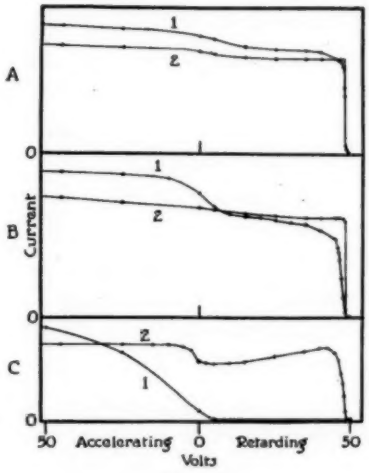

Fig. 2.

The general procedure was as follows. The apparatus was pumped out to a pressure of 10^{-4} to 10^{-5} mm, and the pumps were kept running during all the measurements. An accelerating potential of 50 volts was established between C_1 and the filament, and the temperature of the latter adjusted till a convenient emission resulted. The current through G_2 was then measured with various retarding potentials between C_1 and C_2. When the end of C_2 was replaced by a grid, the plate-current was read on G_3 with various retarding potentials between C_2 and the plate.

Experimental results. The experimental curves are reproduced in Fig. 2. Curve $A(1)$ was obtained with the hole 0.022 cm in diameter. The metal parts were baked out in vacuum at about 400° before

placing in the apparatus, but no attempt was made to reduce the surface layer of copper oxide. The current to cage C_2 is plotted against the retarding or accelerating potential between C_1 and C_2. It is apparent from the curve that about 70% of the electrons (based on the current at zero volts) retain nearly their original velocity. To determine whether low velocity reflection and secondary emission were affecting the distribution, the end of C_1 was now coated with lampblack in a candle flame, since Gehrts[2] has shown that a lampblacked surface is a good absorber for electrons. Curve $A(2)$ shows the result obtained using the same total emission as for curve $A(1)$. About 95% of the electrons have their initial velocity. It is also interesting to note that the actual number of electrons retaining their initial velocity is nearly the same in the two cases, so apparently the only action of the soot is to remove from the beam all those electrons which strike even a glancing blow, thus preventing reflection and secondary emission, and eliminating the low-energy group previously present. Another distribution curve was taken after sooting C_1 and C_2 completely; but the curve was practically the same as $A(2)$, showing that C_2 was an efficient Faraday cage.

These are much better distributions than were obtained by Lehman and Osgood in the experiments above cited. The difference may be due to the higher voltage at which they worked, since it is known that the reflection of electrons from copper increases with the voltage up to 200–300 volts. The nature of the surface as determined by the previous treatment of the copper would also affect the reflection. In some earlier experiments where a crude apparatus was used, in which the metal parts were not baked out, we obtained curves somewhat similar to theirs, but after sooting the copper surfaces the results were as good as with the apparatus described above.

Since, in most of the experiments in electron impact work, the electrons traverse wire gauze grids, an experiment was tried to determine the effect of lampblack under these conditions. The hole in C_1 was replaced by a circular grid of 100 mesh copper gauze 0.5 cm in diameter, while the end of C_2 opposite the plate was replaced by a similar grid 2.5 cm in diameter. Curve $B(1)$ is a distribution curve of the current reaching C_2 in the absence of lampblack. In this case only about 60% of the electrons retained approximately their initial velocity, while the majority of these have suffered a small energy decrease. Curve $B(2)$ shows the distribution after the grids and cages had been

[2] Gehrts, Ann. d. Physik. **36**, 995 (1911).

sooted. It is apparent that about 90% of the electrons have their initial velocity. The absolute magnitudes have no meaning, since the emission was much higher in the second case.

To demonstrate further the effect of carbon, distribution curves of the plate current were taken first without and then with lampblack. These are reproduced in curves $C(1)$ and $C(2)$, respectively, in which the plate current is plotted against the accelerating or retarding voltage between C_2 and P. $C(1)$ is similar to curves obtained by Lawrence[3] with a very short Faraday cage. $C(2)$ shows a much better distribution, but it is poor compared to the curves above, which probably indicates that carbon is not a perfect absorbent. $C(1)$ is plotted to a much smaller current scale than $C(2)$, since the form of the curve and not the magnitude of the current is important.

The authors wish to express their thanks to Dr. G. Glockler for his help and advice; also to the Carnegie Institution of Washington for financial assistance received from a grant made to Prof. A. A. Noyes.

GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY,
PASADENA, CALIFORNIA,
October 29, 1926.

[3] Lawrence, Proc. Nat. Acad. Sci. **12**, 29 (1926).

PHOTOELECTRIC EMISSION AS A FUNCTION OF COMPOSITION IN SODIUM-POTASSIUM ALLOYS

By Herbert E. Ives and G. R. Stilwell

Abstract

The entire series of alloys of sodium and potassium have been investigated with respect to the relative values of the photoelectric currents produced by light polarized with the electric vector in and at right angles to the plane of incidence. The pure metals when molten exhibit values below three for the ratio of the two emissions; the alloys show *three maxima* at compositions approximately 20, 50, and 90 atomic percent of sodium, with values from 10 to 30 for the ratio; the minima between show low values approximating those for the pure metals. The maxima and minima of the ratio of emissions are due to complicated variations in magnitude of the two emissions compared.

ELSTER and Geitel discovered that the photoelectric emission from the liquid equimolecular alloy of sodium and potassium is greatly altered in amount when the plane of polarization of the (obliquely incident) light is varied.[1] They do not appear to have investigated alloys of other proportions than those of the equimolecular one. Pohl and Pringsheim,[2] who studied the photoelectric properties of this alloy, as well as of the pure alkali metals separately, worked under the belief that the high ratio of the emissions occurring when the light is polarized with the electric vector first in, then perpendicular to the plane of incidence (*selective* and *normal* effects) was a characteristic of the pure metals as well. Subsequent work[3] has however shown that pure sodium and potassium, in the liquid form, do not exhibit (at least in the visible spectrum) the high ratio effect found in the equimolecular alloy. It becomes therefore of interest to learn how the photoelectric properties, particularly the ratio of emissions defined above, vary with the relative proportions of sodium and potassium in the alloy.

In order to investigate this question, we made up a series of photoelectric cells of the form shown in Fig. 1. These were simple spherical bulbs made of Pyrex glass and provided with electrodes. An auxiliary side bulb was attached, into which the alloy was introduced first, by distillation, and from which it was poured into the main bulb, — a procedure found advisable for removing any traces of floating impurity.

[1] Elster and Geitel, Ann. d. Physik **LII**, p. 433 (1894).
[2] Pohl and Pringsheim, "Die Lichtelektrischen Ersheinungen" Vieweg (1914).

The alloys were prepared in the distilling system by the following method. Pure sodium and potassium were first distilled in vacuo separately into long pyrex tubes (of about 1 cm diameter). From these tubes, pieces were broken off as nearly as possible of the proper lengths to give the alloy desired. These pieces, after weighing, were introduced into a multiple bulb distilling system attached to the photoelectric cell. The alkali metals were then melted and completely distilled over in vacuo, following the general method and precautions described in earlier papers.[3] After the distilling system was sealed off, the pieces of glass tube which had contained the alkali metals were weighed, and the difference in weight before and after gave the amounts

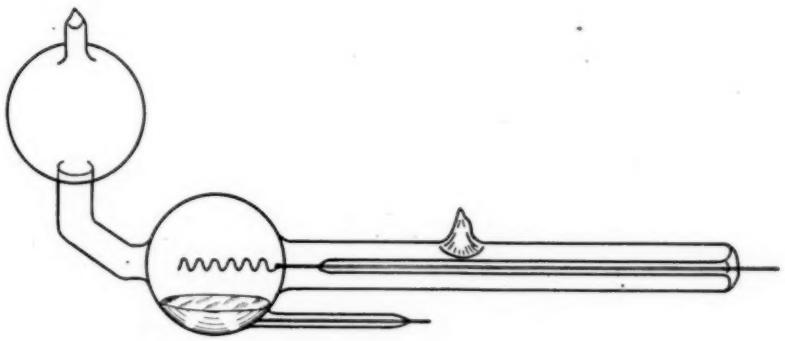

Fig. 1. Type of photoelectric cell used for studying emission characteristics of Na-K alloys.

of alkali metal. Some error is introduced through the crust of oxide which forms at the ends of the columns of alkali metal in the glass tubes. This error can be made relatively small by using tubes of generous length.

Photoelectric currents were excited by the total light of a helical-coil tungsten filament, incident at an angle of 60° after passing through a nicol prism and a lens which focussed an image of the filament on the alloy surface. The cells were operated with 120 volts of applied potential, and the currents were measured on a high-sensibility d'Arsonval galvanometer.

Before giving the results of the measurements it is desirable to discuss some details with regard to the alloys. First of all, it is of extreme importance that the two metals used be pure. The criterion for purity which we have found most useful is really an outcome of this study, and its statement here partially anticipates the conclusion from the

[3] Ives and Johnsrud, Astrophys. J. **LX**, 4, p. 231 (Nov. 1924).

work. The criterion is this: *the ratio of emission defined above for illumination by light incident at 60°, shall be not more than 2 or 3 to 1* for the pure metals when liquid just above their melting points. A very small admixture of either metal with the other greatly increases this ratio. Also it appears probable that other materials than the alkali metals, when present as impurity, may raise the ratio. All our samples of sodium and potassium, after the preliminary distillation, and before being used for the preparation of alloys, were tested by this criterion in a trial cell. It was found that some of the

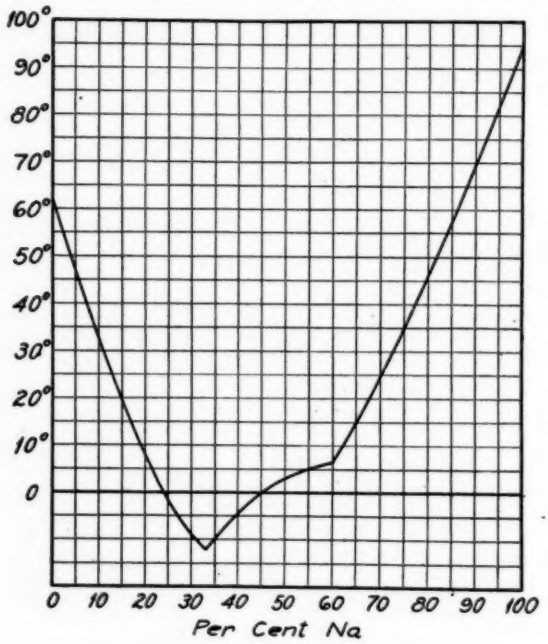

Fig. 2. Melting points of Na-K alloys.

"pure" sodium and potassium obtained from chemical-supply firms fails to meet this test. The greater part of our work has been done with metals from Mallinckrodt, which have uniformly given a low value for the ratio in question.

The physical properties of the Na-K series have already been rather thoroughly studied. The relationship between melting point and composition is given by Kurnakow and Puschin,[4] whose results are shown in Fig. 2, here reproduced for reference. It will be noted that all alloys in the range from 15 to 70 atomic percent of sodium are liquid at room

[4] Kurnakow and Puschin, Zeits. Anorg. Chem. **30**, p. 109 (1902).

temperatures. Since for our purposes the surface must be specular, the alloys in this range are suitable for study at room temperature. The alloys outside this range were warmed just sufficiently to melt them. Through the middle of the range of alloys liquid at room temperatures the liquid appears perfectly homogeneous, not unlike mercury. The alloys on the borderline between the liquid and solid states at room temperatures frequently exhibit a surface structure apparently consisting of floating crystalline plates or of liquid pools separated by projecting thin crystal walls. These crystalline formations sometimes persist as the alloy is cooled, and can frequently be observed in pure slowly-cooled solid sodium and potassium, thus affording nearly specular surfaces suitable for optical measurement.

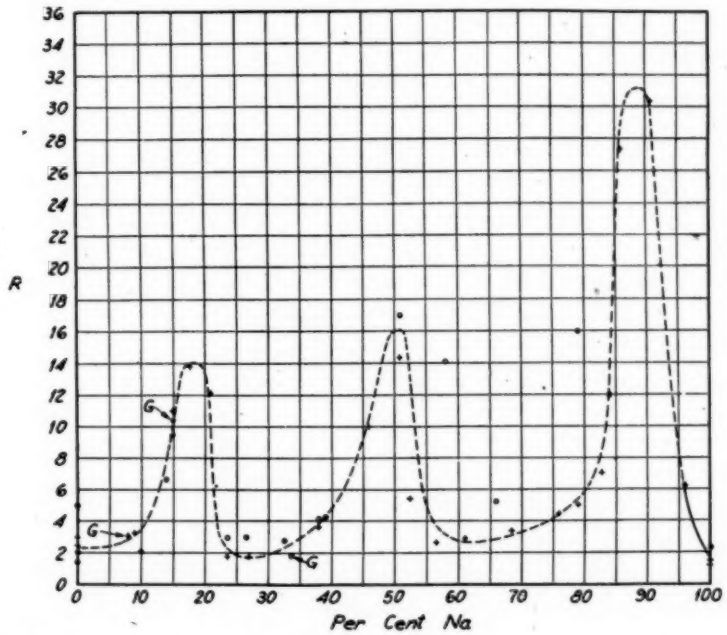

Fig. 3. Ratio of photoelectric emissions for excitation by obliquely incident light polarized in two directions ("selective" and "normal") as a function of atomic percentage of Na in Na-K alloy.

The first series of observations here reported are those made on approximately forty cells of the type of Fig. 1. The results are shown in Fig. 3, where the abscissas represent alloy compositions in atomic percent, the ordinates represent the ratio:

$$R = \frac{\text{emission with electric vector in the plane of incidence}}{\text{emission with electric vector perpendicular to the plane of incidence}}.$$

The outstanding fact is the occurrence of *three maxima*, two close to the ends of the diagram, and one at the middle, corresponding to the equimolecular alloy. Every cell made up is represented in the figure, without regard to the fact that in the earlier cells the quantities of the two metals used were too small to enable us to ascertain the relative proportions as accurately as was later done, resulting in a greater scattering of results and consequent blunting of the maxima. The observations designated by crosses form the group made last, when the technique was most completely developed, and should be given the greatest weight. They indicate that the maxima are quite sharp. Several observations, marked *G*, were made on cells in which the vacuum was imperfect, as shown by the characteristic rapid increase

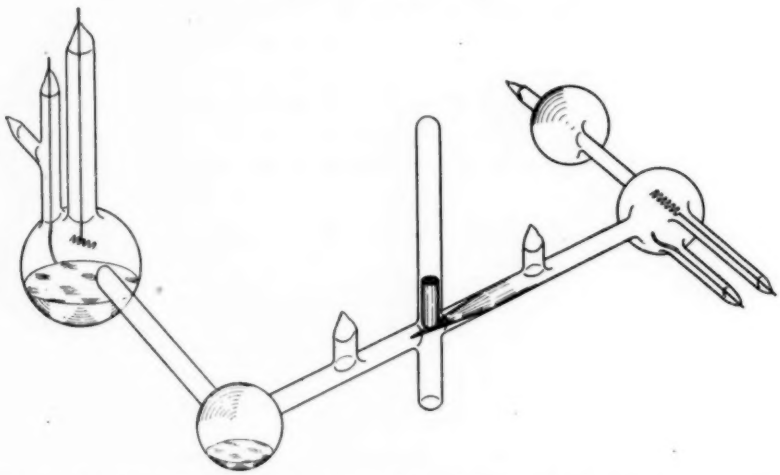

Fig. 4. Special cell used to study complete series of Na-K alloys by successive additions of K (from right-hand bulbs) to Na (in left-hand bulb).

of current with voltage, or by the occurrence of a glow discharge when tested with a spark coil. It will be noted that these cells fall in their proper places on the curve, indicating that the emission ratio R is not affected by the presence of gas.[5]

The data of Fig. 2 show merely the *ratios* of emissions. It is of interest to know how the two emissions in question vary individually.

[5] Fleischer and Dember in Zeits. f. Tech. Phys. **3**, 1926, p. 133, report experiments on potassium in which the emission characteristics of a sealed cell changed with time. The title of their article states that the photoelectric properties are studied with regard to their dependence on gas content. Actually no measurements were made of gas pressure nor was any evidence given that the gas content varied. In the light of our work, it appears to us more probable that the change occurring with time was in the crystalline structure of the surface.

This information cannot be deduced from the measurements on separate cells, each containing different alloys, because of differences in the total emission due to unavoidable variations of conditions occurring in their preparation. In order to determine the emissions in absolute measure, it appeared necessary to construct a cell in which the composition of the alloy could be altered progressively. For this purpose, a double cell was made, as shown in Fig. 4; the two sections were separated from each other by a thin cone-shaped glass diaphragm which could be broken by a falling slug of iron after the two cells had been separately filled with alkali metal and exhausted. Molten metal from one cell could then be allowed to flow by small increments into the other. In order to get an approximate measure of the proportions of the alkali metals present as the mixture proceeded, the bulb selected for the mixing chamber was calibrated beforehand by putting in known volumes of mercury and measuring the dimensions of the mercury pool with a cathetometer. If the meniscus of mercury were the same as that of the Na-K alloys this would afford a reasonably exact measure. Actually the alloys near the sodium end (which were the first produced, potassium being added to an initial small globule of sodium) differ in shape of meniscus quite markedly from mercury, so that the volume measurements were not very satisfactory near the sodium end of the series, and must be taken as merely approximate. (Were the experiment to be repeated, the alloy pool would be photographed in profile and plan, and the volume determined by area measurements of the photographs). The measurements however do show the progressive change in composition sufficiently for the immediate purpose.

The results of this experiment are shown in Figs. 5 and 6. Considering first the behavior of the ratios of emission under the two conditions of polarization (Fig. 5) it appears that the three maxima obtained with the forty individual cells are confirmed. The maxima are not however so sharp, the central maximum is doubled, and is relatively higher and wider, so that the neighboring minima are not so low as in the individual cells. These differences between the behavior of the alloys in separate cells and the progressive mixture are, we believe, to be ascribed to the fact that with the separate cells there was ample time for the alloys to attain equilibrium, while with the series in a single cell the measurements were made immediately after each mixture, and often only a few minutes elapsed before the next step of the series was undertaken.

Considering next the behavior of the two photoelectric currents separately (Fig. 6) we see that the maxima and minima of the ratio are associated with a very complicated course of the two constituent

emissions. Thus taking the "normal" current case "$E \perp$" this exhibits a minimum at approximately 12 atomic percent Na, and a maximum at 25 atomic percent. The maxima and minima in the ratio at 18 and 30 atomic percent are almost entirely due to these variations in

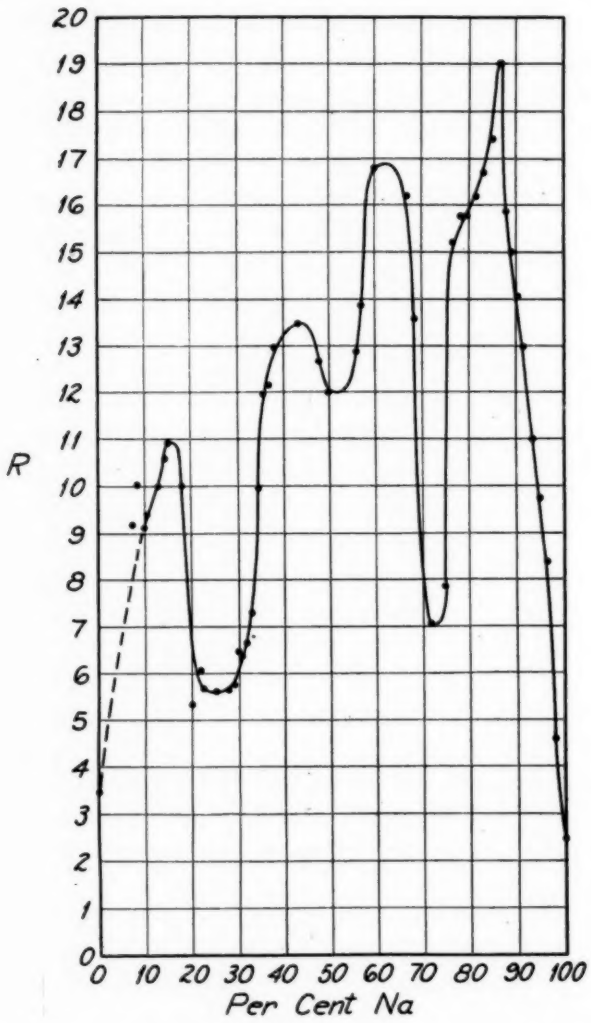

Fig. 5. Ratio of "selective" to "normal" emissions as obtained from series of alloys mixed in cell shown in Fig. 4.

the "normal" current, since the "selective" effect merely shows a practically uniform increase through this region. Toward the other end of the series however, the condition is reversed. While the "normal"

emission ($E \perp$) decreases slowly, the "selective" emission ($E \parallel$) interrupts its gradual rise by a sharp drop and subsequent rise, which accounts for the minimum in the ratio in the neighborhood of 70 atomic percent. It is evident from Fig. 6 that the phenomena are

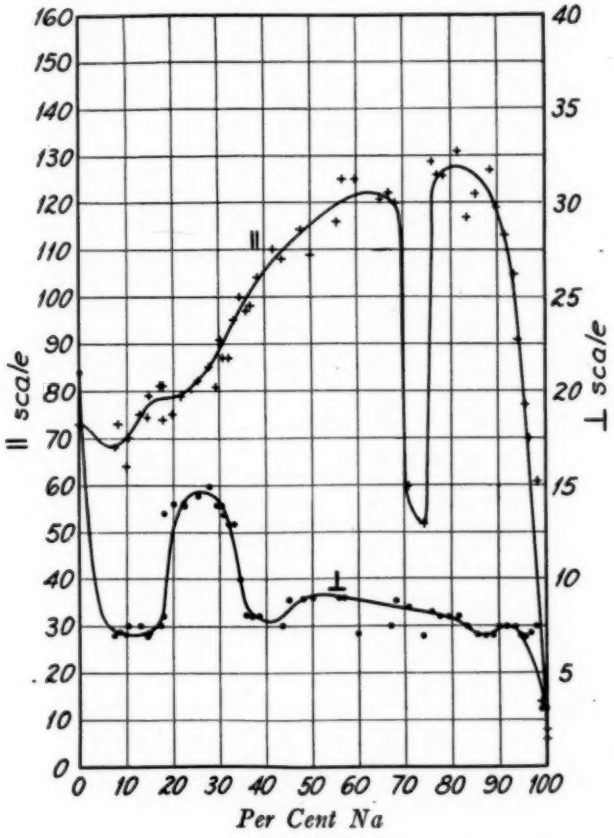

Fig. 6. Variation of "normal" ($\perp$) and "selective" ($\parallel$) emissions as function of Na-K composition, as obtained in cell shown in Figure 4.

quite complex; to obtain complete information, it will be necessary to study the emission with spectrally resolved light. This will be undertaken at an early date.

Discussion

In previous papers, it has been suggested that the great difference in photoelectric emission which occurs in certain cases when the plane of polarization of the exciting light is varied, is to be attributed to a regular orientation of the surface atoms or molecules. The results

of the present study may be interpreted in the same way if we consider the sodium and potassium atoms as forming a series of atomic groups, as the relative proportions of the metals vary. Certain of these groups may be pictured as consisting of chains or other structures which will tend to become oriented in definite ways at the liquid surfaces, and to respond differently according to the direction of the electric vector with respect to the surface. The coincidence of the central maximum with the composition KNa, supposed to be a metallic compound, is suggestive. There appears however to be no other correlation with either integral atomic proportions, or with other physical properties as indicated by the melting point data. A possible working hypothesis is that the maxima close to the two ends of the series are to be ascribed to surface layers of unit atomic thickness of potassium or sodium. Further light may be obtained on these questions by studying the distribution of response through the spectrum.

In a previous study of a sodium-potassium alloy,[3] support was found for the hypothesis of orientation of the surface atoms or molecules by the fact that the ratio of emissions was greatly reduced in value when the alloy was heated. This observation has been completely confirmed in the present work by numerous observations on alloys all through the series, which however need not be shown, since they are adequately represented by the data shown in the earlier paper. The evidence for the existence of orientations of atoms at the surface has been supplemented in the present work by the actual observation of crystalline planes on the surface of semi-molten alloys, as already mentioned. The selective-normal ratio of emissions from these crystalline surfaces is in all cases higher than from the same material when completely melted. Further evidence of the same sort is obtained from the observation that pure sodium may solidify with flat specular areas, and these, unlike the previously observed specular solid potassium,[3] and unlike molten sodium, show relatively high ratios (7 to 8) for the selective-normal ratio. These high values rapidly drop as the temperature of the solid sodium is raised, approaching the molten value (2-3) continuously. The high ratios found in smooth solid sodium increase as the cell stands, suggesting an increasing crystalline character of the surface.

It may be noted that the conclusion drawn in an earlier paper[3] that sodium-potassium alloy is the only one of the alkali metal alloys which has a high selective-normal ratio may be subject to revision in the light of the new results on Na-K allloy It is possible that alloys

of the other alkali metals, in different proportions than those thus far studied will show high values for this ratio.[6]

We desire in conclusion to acknowledge our indebtedness to Mr.A. L. Johnsrud for his aid in the volume measurements used to determine the alloys compositions.

BELL TELEPHONE LABORATORIES, INCORPORATED
NEW YORK, N. Y.
October 11, 1926.

[6] Another factor contributing to the occurrence of high ratios has been found since the work here described was completed. This is a failure of the proportionality between photoelectric current and illumination for the "normal" emission. This will be treated in a later paper.

THE SYMMETRICAL TOP IN THE UNDULATORY MECHANICS[1]

By R. de L. Kronig and I. I. Rabi

Abstract

Schrödinger's method for determining the energy levels of an atomic system is applied to the case of the symmetrical top (moment of inertia about axis of symmetry C, the other one A). The energy values are found to be

$$W_{jn} = \frac{h^2}{8\pi^2}\left[\frac{1}{A}\, j(j+1) + \left(\frac{1}{C} - \frac{1}{A}\right)n^2\right]$$

in agreement with the result obtained by Dennison from the matrix mechanics. The quantum numbers j and n must be integers restricted by $0 \leqq j, |n| \leqq j$, while half-integral values are not permissible. The intensities of transitions are also calculated.

Introduction

THROUGH the important work of Schrödinger[2] the problem of finding the energy levels of an atomic system has been reduced to the determination of the characteristic values of a certain second order partial differential equation for a function U of the generalized coordinates, the so-called wave equation. It is the purpose of this paper to apply his procedure to the case of the symmetrical top, a mechanical system useful in the interpretation of molecular spectra. Dennison[3] has obtained the energy values and intensities of this system in terms of three quantum numbers, j, n, m on the basis of the matrix mechanics. He has, however, only shown that his solution satisfies certain conditions following directly from the fundamental equations of the matrix mechanics without proving that all these equations are obeyed themselves, although a comparison with the amplitudes of the top in the classical theory made it probable that his results are entirely satisfactory. Moreover the question remained unsettled whether j and n had to be given integral or half integral values. For these reasons a treatment of the same problem by Schrödinger's method does not appear superfluous.

[1] See the preliminary note, Nature **118**, 805 (1926). In a paper which came to our attention after this article was sent in for publication F. Reiche, (Zeit. f. Phys. **39**, 444, 1926), also investigates the energy values of the symmetrical top by the same method and arrives at results identical with ours. He does not, however, treat the intensities, and therefore it was thought worth while to publish our results.

[2] E. Schrödinger—Ann. d. Phys. **79**, 361, 489, 734, (1926).

[3] D. Dennison—Phys. Rev. **28**, 318, (1926).

THE WAVE EQUATION AND ITS SEPARATION

Schrödinger's wave equation states that

$$\Delta U+\frac{8\pi^2}{h^2}(W-V)U=0, \tag{1}$$

where Δ denotes the gradient of the divergence in the non-Euclidean configurational space and $V(q^i)$ the potential energy of the system under consideration. The question to be answered is: For what values of the constant W do solutions U exist which are finite throughout the configurational space (and zero at infinity if the space extends to infinity)? These values W shall represent the energies of the stationary states.

To describe the motion of the symmetrical top we shall use Euler's angles θ, ϕ, ψ; θ denoting the angle between the z-axis in space and the axis of symmetry z' of the top, ϕ and ψ the angles between the line of nodes (line of intersection between the x'- and x-axes respectively). The kinetic energy in terms of the generalized momenta is given by

$$2T=\frac{1}{A}p_\theta^2+\left(\frac{\cos^2\theta}{A\sin^2\theta}+\frac{1}{C}\right)p_\phi^2+\frac{1}{A\sin^2\theta}p_\psi^2-\frac{2\cos\theta}{A\sin^2\theta}p_\phi p_\psi,$$

A and C being the moments of inertia of the top about the x'- and z'-axes respectively. For our system the partial differential equation (1) for U becomes

$$\frac{\partial^2U}{\partial\theta^2}+\frac{\cos\theta}{\sin\theta}\frac{\partial U}{\partial\theta}+\left(\frac{A}{C}+\frac{\cos^2\theta}{\sin^2\theta}\right)\frac{\partial^2U}{\partial\phi^2}+\frac{1}{\sin^2\theta}\frac{\partial^2U}{\partial\psi^2}$$
$$-\frac{2\cos\theta}{\sin^2\theta}\frac{\partial^2U}{\partial\phi\partial\psi}+\frac{8\pi^2AW}{h^2}U=0. \tag{2}$$

This equation will be separated by the substitution

$$U=\Theta(\theta)\begin{cases}\sin(n\phi+m\psi)\\ \cos(n\phi+m\psi)\end{cases} \tag{3}$$

where $\Theta(\theta)$ is a function of θ alone. It is necessary that U returns to the same value if ϕ and ψ are increased by integral multiples of 2π, since then the mechanical system takes up the same position. This can only be accomplished by having the constants n and m equal to

integers. Substituting (3) in Eq. (2) gives an ordinary second order differential equation for Θ

$$\frac{d^2\Theta}{d\theta^2}+\frac{\cos\theta}{\sin\theta}\frac{d\Theta}{d\theta}-\frac{(m-n\cos\vartheta)^2}{\sin^2\theta}\Theta+\sigma\Theta=0, \tag{4}$$

$$\sigma=\frac{8\pi^2AW}{h^2}-\frac{A}{C}n^2. \tag{5}$$

Determination of the Characteristic Values[4]

Eq. (4) can be transformed into the hypergeometric equation by a suitable change of variables. We shall introduce the following notation:

$$\lambda_1\begin{cases}\frac{1}{2}(m+n)\\ -\frac{1}{2}(m+n)\end{cases}\quad\lambda_2\begin{cases}\frac{1}{2}(m-n)\\ -\frac{1}{2}(m-n)\end{cases}\quad\lambda_3=\frac{1}{2}+\left(\frac{1}{4}+\sigma+n^2\right)^{1/2}\quad\mu_3=\frac{1}{2}-\left(\frac{1}{4}+\sigma+n^2\right)^{1/2} \tag{6}$$

The brackets in the first two expressions mean that λ_1 and λ_2 shall be so chosen from the two quantities behind the bracket that $\lambda_1\geqq 0$, $\lambda_2\geqq 0$; e. g. if $(m+n)\geqq 0$, $(m-n)\leqq 0$, then $\lambda_1=\frac{1}{2}(m+n)$, $\mu_1=-\frac{1}{2}(m+n)$, $\lambda_2=-\frac{1}{2}(m-n)$, $\mu_2=\frac{1}{2}(m-n)$. Furthermore we introduce in Eq. (4) the new independent variable

$$x=\frac{1}{2}(\cos\theta+1) \tag{7}$$

and the new dependent variable

$$X=x^{-\lambda_1}(x-1)^{-\lambda_2}\Theta. \tag{8}$$

Eq. (4) then takes the form of the hypergeometric equation

$$x(1-x)\frac{d^2X}{dx^2}+[\gamma-(\alpha+\beta+1)x]\frac{dX}{dx}-\alpha\beta X=0, \tag{9}$$

where

$$\alpha=\lambda_1+\lambda_2+\lambda_3,\qquad \beta=\lambda_1+\lambda_2+\mu_3,\qquad \gamma=2\lambda_1-1. \tag{10}$$

From these and our choice of λ_1 and λ_2 it follows always that

$$\gamma-1=2\lambda_1\geqq 0,\qquad \alpha+\beta-\gamma=2\lambda_2\geqq 0.$$

Moreover $\gamma-1=p$, where p is an integer $\geqq 0$.

[4] See L. Schlesinger—Differentialgleichungen, (Sammlung Schubert No. 13, Göschen 1900, Chapter 4.)

To the interval of our old variable θ from 0 to π there corresponds the interval from 0 to 1 of the new variable x. From Eq. (8) it follows that if Θ is to be finite in this interval including the limits, then (since λ_1 and $\lambda_2 \geqq 0$) X must be regular inside this interval and at the limits must not become infinite of higher order than $x^{-\lambda_1}$ and $(x-1)^{-\lambda_2}$.

The solution of Eq. (9) is expressible in terms of hypergeometric series. We know that $\gamma - 1 = p$, where p is zero or a positive integer. We distinguish the following cases:

(a). If $p > 0$ and neither α nor β is equal to one of the numbers $1 \cdots p$; or if $p = 0$ and neither α nor β is equal to zero, then two independent particular solutions in the neighborhood of $x = 0$ are given by

$$X_1 = F(\alpha,\beta,\gamma,x),$$
$$X_2 = G(\alpha,\beta,\gamma,x) + F(\alpha,\beta,\gamma,x) \log x,$$

where

$$F(\alpha,\beta,\gamma,x) = 1 + \frac{\alpha \cdot \beta}{1 \cdot \gamma} x + \frac{\alpha(\alpha+1)\beta(\beta+1)}{1 \cdot 2\gamma(\gamma+1)} x^2 + \cdots$$

is the hypergeometric series, and G is a series

$$G(\alpha,\beta,\gamma,x) = x^{1-\gamma} \sum c_k x^k, \qquad c_0 \neq 0.$$

(b). If $p > 0$ and at least one of the quantities α or β is equal to one of the quantities $1 \cdots p$, then

$$X_1 = F(\alpha,\beta,\gamma,x),$$
$$X_2 = x^{1-\gamma} F(\alpha + 1 - \gamma, \beta + 1 - \gamma, 2 - \gamma, x).$$

In the second series the zero factors in the numerators and denominators of the coefficients are to be omitted.

(c). If $p = 0$ and at least one of the quantities α and β is zero, then

$$X = \text{Const.}$$

will be a solution.

We see that there are no solutions Θ fulfilling the requirements of finiteness inside the interval unless at least one of the quantities α and β is zero or a negative integer. For if that is the case, the solution X_1 will have only a finite number of terms and hence be finite throughout the interval. However, if neither α not β is a negative integer or zero, X_1 will become infinite for $x = 1$, since $F(\alpha, \beta, \gamma, x)$ diverges for $x = 1$ if, as in our case, the real part of $\gamma - \alpha - \beta \leqq 0$, becoming infinite as $(1-x)^{\gamma-\alpha-\beta} = (1-x)^{-2\lambda_2}$ (or as $\log (1-x)$ if $\gamma - \alpha - \beta = 0$). The

solution X_2 on the other hand becomes infinite as $x^{1-\gamma}=x^{-2\lambda_1}$ (or as $\log x$ if $1-\gamma=0$).

From Eq. (6) and Eq. (10) it follows that if α and β are real, $\alpha \geqq \beta$ so that for convergence β must be zero or a negative integer. That will only be the case if

$$\sigma=j(j+1)-n^2, \qquad j=(\lambda_1+\lambda_2),(\lambda_1+\lambda_2+1)\cdots, \tag{11}$$

as is easily seen from (6) and (10). Hence j must be a positive integer or zero since $\lambda_1+\lambda_2$ is always a positive integer or zero. As a direct consequence of the condition expressed in Eq. (11),

$$j \geqq \lambda_1+\lambda_2,$$

we have

$$j \geqq |n|, \qquad j \geqq |m|, \tag{12}$$

since, according to the definition (6) of λ_1 and λ_2, $(\lambda_1+\lambda_2)$ is always the larger of the two quantities $|n|$ and $|m|$.

Introducing our value σ into Eq. (5) we get for the energy levels

$$W_{jn}=\frac{h^2}{8\pi^2}\left[\frac{1}{A}j(j+1)+\left(\frac{1}{C}-\frac{1}{A}\right)n^2\right]$$

in harmony with Dennison's[3] results, but with the additional information that j and n must be integers. The requirements (12) shows that for a given j and n there exist $2j+1$ values of m. This $(2j+1)$-fold occurrence of the value W_{jn} among the characteristic value of the wave equation corresponds to the fact that the state (j, n) will divide into $(2j+1)$ levels under the action of an external field. The quantum number j determines the total moment of momentum, n the moment of momentum about the axis of symmetry.

Calculation of Intensities

As shown by Schrödinger[2] and Eckart[5] the matrix elements of the coordinate q^i in the Born-Heisenberg mechanics are given by

$$q^i(k,l)=C_kC_l\int dv q^i U_k U_l, \tag{13}$$

where U_k and U_l are the characteristic functions belonging to the states k and l respectively, while dv is the element of volume of the

[5] C. Eckart—Phys. Rev. **28**, 711, (1926).

configurational space. The integration extends over the whole domain of the variables. C_k is defined by

$$C^2_k \int dv U^2_k = 1. \tag{14}$$

If in our problem we consider a radiating charge attached to the top such that its coordinates in the system of axes x', y', z' rigidly connected to the top are a, 0, c, then its coordinates in space are given by

$$\begin{aligned} x &= c \sin\theta \sin\psi + a \cos\phi \cos\psi - a \cos\theta \sin\phi \sin\psi, \\ y &= -c \sin\theta \cos\psi + a \cos\phi \sin\psi + a \cos\theta \sin\phi \cos\psi, \\ z &= c \cos\theta + a \sin\theta \sin\phi. \end{aligned}$$

We have but to substitute these and our characteristic functions in Eqs. (13) and (14) and to evaluate the definite integrals.

As an example we shall take the coordinate z. For the matrix element corresponding to the transition $j, n, m - j', n', m'$ we find with the aid of Eq. (13)

$$\begin{aligned} z(j,n,m\,;j',n',m') = C_{jnm}C_{j'n'm'} \int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi} A(C)^{1/2} \sin\theta d\theta d\phi d\psi \\ \cdot (c\cos\theta + a\sin\theta\sin\phi)\Theta(j,n,m,\theta)\Theta(j',n',m',\theta) \\ \cdot \begin{cases} \sin(n\phi + m\psi) \\ \cos(n\phi + m\psi) \end{cases} \begin{cases} \sin(n'\phi + m'\psi) \\ \cos(n'\phi + m'\psi) \end{cases} \end{aligned}$$

the volume element dv in the non-Euclidean space being given by

$$dv = (g)^{1/2} d\theta d\phi d\psi = A(C)^{1/2} \sin\theta d\theta d\phi d\psi.$$

It is immediately evident that due to the integration over ϕ and ψ $z(j, n, m; j', n', m')$ will be different from zero only when $n' = n$, $n' = n \pm 1$ and $m' = m$. These conditions correspond to the well-known selection rules for the radiation emitted by the top. It will be sufficient for the purpose of illustration to restrict ourselves now to the case $n' = n$. We then have

$$\begin{aligned} z(j,n,m\,;j',n,m) = 4\pi^2 c C_{jnm}C_{j'nm}A(C)^{1/2} \\ \cdot \int_0^{\pi} d\theta \sin\theta\Theta(j,n,m,\theta)\Theta(j',n,m,\theta). \end{aligned} \tag{15}$$

For C_{jnm} we integrate over ϕ and ψ in Eq. (14) and obtain

$$4\pi^2 A(C)^{1/2} C_{j'nm}^2 \int_0^\pi d\theta \sin\theta \Theta^2(j,n,m,\theta) = 1 \tag{16}$$

and similarly for $C_{j'nm}$.

We now proceed with the evaluation of the integrals. Expressing Θ in terms of the hypergeometric series according to Eqs. (7) and (8) and writing

$$\beta = -\nu, \qquad \alpha = \epsilon + \nu, \tag{17}$$

where ν is a positive integer or zero, we get for the first integral

$$I_1 = \int_0^\pi d\theta \sin\theta \cos\theta \Theta(j,n,m,\theta)\Theta(j',n,m,\theta)$$

$$= (-1)^{\epsilon-\gamma} \int_0^1 dx(1-2x)F(\epsilon+\nu, -\nu, \gamma, x)F(\epsilon+\nu', -\nu', \gamma, x)x^{\gamma-1}(1-x)^{\epsilon-\gamma}.$$

Both ϵ and γ are the same in the two functions F, since they are given by

$$\epsilon = 2(\lambda_1 + \lambda_2) + \lambda_3 + \mu_3, \quad \gamma = 2\lambda_1 - 1$$

according to Eqs. (10) and (17), and are hence independent of j according to Eq. (6).

All integrals occurring in this and the remaining calculations can be reduced to the general form

$$\int_0^1 dx F(\epsilon+\nu, -\nu, \gamma, x)F(\epsilon'+\nu', -\nu', \gamma', x)x^{\gamma-1}(1-x)^{\epsilon-\gamma} \tag{18}$$

by means of the relation valid for any hypergeometric series

$$xF(\epsilon+\nu, -\nu, \gamma, x) =$$

$$\frac{(\gamma-1)(\gamma-2)}{(\epsilon+\nu-1)(\nu+1)}[F(\epsilon+\nu-1, -\nu-1, \gamma-1, x) - F(\epsilon+\nu-1, -\nu-1, \gamma-2, x)]$$

Multiplying the differential equation (9) for $F(\epsilon+\nu, -\nu, \gamma, x)$, which in our new notation is

$$x(1-x)F'' + [\gamma - (\epsilon+1)x]F' = -\nu(\nu+\epsilon)F, \tag{19}$$

by $x^{\gamma-1}(1-x)^{\epsilon-\gamma}$, it is seen that

$$-(\epsilon+\nu)\nu F x^{\gamma-1}(1-x)^{\epsilon-\gamma} = \frac{d}{dx}[F' x^\gamma (1-x)^{\epsilon-\gamma+1}]. \tag{20}$$

Substituting $F(\epsilon+\nu,-\nu,\gamma,x)$ from this relation in (18) and integrating by parts we get

$$\frac{1}{\nu(\epsilon+\nu)}\int_0^1 dx F'(\epsilon+\nu,-\nu,\gamma,x)F'(\epsilon'+\nu',-\nu',\gamma',x)x^{\gamma}(1-x)^{\epsilon-\gamma+1}.$$

This procedure can be continued by differentiating Eq. (19) and getting a relation similar to Eq. (20) with F' and F'' instead of F and F'. Since the F's are polynomials in x it is thus possible to reduce the integral (18) after a finite number of steps to the form

$$\text{const.}\int_0^1 dx\cdot x^p(1-x)^q = \frac{\text{const.}\,p!q!}{(p+q+1)!}.$$

In our example I_1 vanishes except when $\nu'=\nu\pm1$, $\nu'=\nu$ or $j'=j\pm1$, $j'=j$. This result represents the selection rule for j. If $\nu'=\nu$ i. e. $j'=j$, then

$$I_1 = \frac{2(-1)^{\epsilon-\gamma}\nu![(\gamma-1)!]^2(\epsilon+\nu-\gamma)!(\epsilon-1)(\epsilon-2\gamma+1)}{(\gamma+\nu-1)!(\epsilon+\nu-1)!(\epsilon+2\nu)(\epsilon+2\nu-1)(\epsilon+2\nu+1)}.$$

The integral in Eq. (16) is evaluated in the same fashion and gives

$$C_{j^2nm} = -\frac{(-1)^{\epsilon-\gamma}(\gamma+\nu-1)!(\epsilon+\nu-1)!(\epsilon+2\nu)}{8\pi^2A(C)^{1/2}\nu![(\gamma-1)!]^2(\epsilon+\nu-\gamma)!}.$$

Then from Eq. (18)

$$z(j,n,m\,;j,n,m) = -c\frac{(\epsilon-1)(\epsilon-2\gamma+1)}{(\epsilon+2\nu-1)(\epsilon+2\nu+1)} = c\frac{nm}{j(j+1)}.$$

This agrees with Dennison's[3] expression, our notation j, n, m corresponding to his m, n, σ. In the same way the other intensities are computed. They too are found to agree with Dennison's values except that the quantities called by him $B^{m\ n\ \sigma}_{m\ n-1\ \sigma\mp1}$ and $B^{m\ n\ \sigma}_{m-1\ n-1\ \sigma\mp1}$ must be

$$\left(B^{m\,n\ \sigma}_{m\,n-1\,\sigma\mp1}\right)^2 = \frac{(m\pm\sigma)(m\mp\sigma+1)(m+n)(m-n+1)}{16m^2(m+1)^2},$$

$$\left(B^{m\ n\ \sigma}_{m-1\,n-1\,\sigma\mp1}\right)^2 = \frac{(m\pm\sigma)(m\pm\sigma-1)(m+n)(m+n-1)}{64m^2(m^2-\frac{1}{4})},$$

a difference probably due to a misprint arising from the inversion of two $\pm$ signs.

DEPARTMENT OF PHYSICS,
COLUMBIA UNIVERSITY,
November 4, 1926.

THE ENERGY OF THE CROSSED-ORBIT MODEL OF THE HYDROGEN MOLECULE

By Elmer Hutchisson

Abstract

Computations are made with the classical quantum theory to determine the energy of a model of the hydrogen molecule similar to the crossed-orbit model of the helium atom with the nucleus divided and separated into two parts. In the preliminary computations the repelling force between the diametrically opposed electrons is neglected, allowing the masses and the charges of the two electrons to be lumped together. This reduces the problem from one of four bodies to one of three bodies and the computations follow those made by Pauli on the H_2 ion except that the mass and charge of the electron are doubled. The effect of the interaction is then obtained in a manner similar to that used by Kramers for the helium atom. In this method terms with undetermined coefficients are introduced into the perturbing potential. The coefficients are then determined so as to reduce the square of the ratio of the perturbing force to the real force to a minimum. Applying this method to the crossed-orbit model of the hydrogen molecule, the energy of the normal state is found to be 45.2 volts. This value is much higher than that given by experiment (31.42 volts), so that it is necessary to conclude that according to the older quantum theory the model does not correspond with reality.

I. Introduction

THE hydrogen molecule consists of four bodies, two positively charged nuclei and two electrons. The dynamical problem of the determination of the energy of the stationary state of lowest energy cannot be solved completely unless certain assumptions are made. The highly symmetrical circle model proposed by Bohr[1] in 1913, must be discarded since it is unstable and since its energy values do not agree with experiment. Other models may be devised by analogy with the slightly simpler problems of three bodies, the hydrogen molecule ion and the neutral helium atom. The former problem has been investigated with great completeness independently by Pauli[2] and Niessen.[3] All types of orbits have been considered. The orbits lying in a fixed plane containing the axis are not discussed in detail, partly because they are unstable and partly because the electrons come arbitrarily close to the nuclei. The other or spacial orbits fall into three classes, the orbits of the mid-plane, those symmetrical with respect to the mid-plane, and

[1] For details see—Sommerfeld—Atombau, Appendix 14.
[2] W. Pauli Jr., Ann. der Phys. 68, 177 (1922).
[3] K. F. Niessen, Doctor's Dissertation, Utrecht (1922); Ann. der Phys. 70, 129 (1923).

those which are unsymmetrical. Those orbits which lie in the mid-plane (including the Bohr circular orbit) are unstable with respect to a small displacement perpendicular to the plane.[4] The orbits of the symmetrical class are proved dynamically stable while the question is left unanswered for those inherently improbable orbits, the unsymmetrical class.

The orbit of smallest energy of the symmetrical class, which should represent the normal ionized hydrogen molecule, consists of a multiply periodic orbit on the surface of an ellipsoid of revolution. We can obtain an approximate idea of the path of the electron by imagining a sine wave wrapped around an ellipsoid of revolution which has the two nuclei as foci. The energy and constants of this orbit have been computed both by Pauli and by Niessen.

Considering the other three body problem, that of the neutral helium atom we find a larger variety of models has been proposed.[5] In the crossed-orbit model of helium it is assumed that the orbits of the two electrons are of the same size and shape but inclined at approximately 120° to each other. The energy and dimensions of this model have been determined independently by J. H. Van Vleck[6] and H. A. Kramers.[7]

Since in general we may obtain a model for the hydrogen molecule by splitting the helium nucleous into two parts and separating them, we would expect, as was suggested by M. Born[8] in 1922, a hydrogen molecule model corresponding to the crossed-orbit model of helium. The orbits, neglecting the interaction of the electrons, would resemble those of the hydrogen molecule ion deduced by Pauli and Niessen and the perturbations due to the interaction of the electrons may be obtained in a manner similar to that used by Kramers for the helium atom. It is the purpose of this paper to make calculations for this crossed-orbit model of the hydrogen molecule.

II. Investigation of the Mechanical System

In the crossed-orbit model the nuclei determine the axis giving the well known dumb-bell form usually associated with diatomic molecules. The electrons travel about this axis in orbits which intersect at about

[4] In spite of this fact, H. C. Urey (Phys. Rev. **27**, 216 (1926)) has recently made some computations with these orbits and obtains agreement with one interpretation of the work of Olson and Glockler but the results are not very convincing.

[5] For complete discussion see J. H. Van Vleck, Quantum Principles and Line Spectra, Bull. N. R. C. No. 54, p. 86 (1926).

[6] J. H. Van Vleck, Phil. Mag. **44**, 842 (1922).

[7] H. A. Kramers, Zeits. f. Physik. **13**, 312 (1923).

[8] M. Born, Die Naturwissenschaften **10**, 677 (1922).

120°. For preliminary computations we may reduce our problem to one of three bodies by neglecting the repelling force of the two electrons. In this way the relative position of the electrons is immaterial and the two electrons may be lumped together into a body with two units of charge and mass. The mathematics needed in this case follows closely that used by Pauli in the H_2 ion with the exception that the mass and charge of the electron are doubled. In this section, we shall use both Z and Z' as the charge on the nuclei. In the preliminary work, $Z = Z' = 1$, so that the distinction is of no consequence.

The possibility of treating this system of two nuclei and one electron as conditionally periodic, depends essentially upon the fact that the nuclei may be considered stationary. This approximation is sufficient for our purpose since the mass of the electron is small compared to that of the nuclei and the contribution to the total energy due to motion of the nuclei is also small.

In the problem of two attracting centers, the variables of the Hamilton-Jacobi partial differential equation may be separated by means of elliptical coordinates. Let r_1 and r_2 represent the distances of the electron from the nuclei, $2c$ be the distance between the nuclei, ρ be the distance of the electron from the axis and ϕ be the azimuth about the axis. The elliptical coordinates are defined by

$$\lambda = (r_1 + r_2)/2c \qquad \mu = (r_1 - r_2/2c \tag{1}$$

The curves, $\lambda =$ constant, form a family of confocal ellipses while those, for which $\mu =$ constant, form confocal hyperbolas with the nuclei as foci. From the definition it follows that $\lambda \geqq 1$ and $-1 \leqq \mu \leqq +1$. The distance from the axis is given by

$$\rho = c[(\lambda^2 - 1)(1 - \mu^2)]^{1/2} \quad \text{and} \quad z = c\lambda\mu \tag{2}$$

where z is the distance of the electron above the mid-plane. We may now write for the potential energy

$$E_{\text{Pot}} = -\frac{2Z'e^2}{r_1} - \frac{2Z'e^2}{r_2} + \frac{Z^2e^2}{2c} = -\frac{4Z'e^2}{c}\frac{\lambda}{(\lambda^2 - \mu^2)} + \frac{Z^2e^2}{2c} \tag{3}$$

and for the kinetic energy

$$E_{\text{Kin}} = m(\dot{z}^2 + \dot{\rho}^2 + \rho^2\dot{\phi}^2). \tag{4}$$

We then obtain for the Hamiltonian function

$$H = \frac{1}{4c^2m(\lambda^2 - \mu^2)}\left[(\lambda^2 - 1)p_\lambda^2 + (1 - \mu^2)p_\mu^2 + \left(\frac{1}{\lambda^2 - 1} + \frac{1}{1 - \mu^2}\right)p_\phi^2\right] - \frac{4Z'e^2}{c}\frac{\lambda}{\lambda^2 - \mu^2} + \frac{Z^2e^2}{2c} = W \tag{5}$$

and we may let $W-(Z^2e^2/2c)=-\alpha_1/4c^2m$ thus defining α_1. Since ϕ does not occur in the Hamiltonian function p_ϕ is a constant and we set $p_\phi=\alpha_3$ ($\phi=$cyclic coordinate). We may now separate the variables in equation (5), giving

$$p_\lambda = [F(\lambda)\alpha_1]^{1/2}/(\lambda^2-1) \tag{6}$$

where

$$F(\lambda) = (-\lambda^2+B\lambda+C)(\lambda^2-1)-A = -\lambda^4+B\lambda^3 + (1+C)\lambda^2-B\lambda-(A+C).$$

and

$$A=\alpha_3^2/\alpha_1 \qquad B=16e^2cmZ'/\alpha_1 \qquad C=\alpha_2/\alpha_1. \tag{7}$$

Likewise

$$p_\mu = [G(\mu^2)\alpha_1]^{1/2}/(1-\mu^2) \tag{8}$$

where

$$G(\mu^2) = (\mu^2-C)(1-\mu^2)-A = -\mu^4+(1+C)\mu^2-(A+C).$$

Now

$$W = -\frac{\alpha_1}{4c^2m}+\frac{Z^2e^2}{2c} = -\frac{4e^2}{c}\frac{Z'}{B}+\frac{Z^2e^2}{2c} = -\frac{e^2}{2c}\left[\frac{8Z'-BZ^2}{B}\right]. \tag{9}$$

To quantize this motion we apply the Wilson-Sommerfeld rule that $\oint p_k dq_k = n_k h = J_k$. In our problem we have

$$J_1 = \oint p_\lambda d\lambda \qquad J_2 = \oint p_\mu d\mu \qquad J_3 = \int_0^{2\pi} p_\phi d\phi$$

and then

$$J_1 = n_1 h \qquad J_2 = n_2 h \qquad J_3 = n_3 h.$$

Another necessary condition is that for the equilibrium of the nuclei. We may state this condition thus—the forces acting on the nuclei must vanish when averaged over a period. In Pauli's paper it is proved that this condition is satisfied when the virial law for Coulomb forces is fulfilled. This relation states that $2E_{\text{kin}}=-E_{\text{pot}}$ on the time average or in other words

$$\overline{E_{\text{pot}}} = 2W \quad \text{since} \quad W = E_{\text{pot}}+E_{\text{kin}}. \tag{10}$$

In this paper we are interested primarily in the orbit of smallest energy. It is proved in Pauli's paper that the orbit of smallest energy is the orbit with the smallest quantum numbers. The smallest value of

the azimuthal quantum number n_3 is unity, since $n_3=0$ would give an orbit of the plane containing the axis, which has already been excluded. Likewise, n_2 the quantum number associated with the μ coordinate cannot equal zero for in this case we would have $\mu=$constant which is impossible for the symmetrical class of orbits. The orbit of smallest energy has therefore the quantum numbers 0, 1, 1. In reality we are assuming that the quantum numbers are 0, $\frac{1}{2}$, $\frac{1}{2}$ for each electron since we have two electrons. The orbit of the electron is therefore a multiply periodic orbit on the surface of an ellipsoid of revolution generated when the ellipse $\lambda=$constant is rotated about the axis. The setting of λ equal to a constant simplifies the Hamilton-Jacobi equation since $p_\lambda=0$.

We must now obtain an expression for the time mean value of any quantity averaged over the orbit of the electron. Suppose we consider a quantity Q, the time mean value of this quantity is given by

$$\overline{Q} = \oint Q dt / \oint dt \tag{11}$$

where the integration is carried over a complete period.

Using the Hamilton canonical equations and from Eqs. (5) and (8), we obtain for the time mean value of any quantity

$$Q = \oint Q(\lambda^2 - \mu^2)[G(\mu^2)]^{-1/2} d\mu / \oint (\lambda^2 - \mu^2)[G(\mu^2)]^{-1/2} d\mu. \tag{12}$$

We can apply this equation to the nuclear equilibrium condition (10). From (3) it is clear that in our present case the potential energy is given by

$$E_{\text{pot}} = -\frac{4e^2}{c}\frac{\lambda}{\lambda^2 - \mu^2} + \frac{e^2}{2c}.$$

Making use of this equation and (9), Eq. (10) becomes

$$\overline{\frac{\lambda}{\lambda^2 - \mu^2}} = \frac{1}{8}\left[\frac{16 - 2B}{B} + 1\right] = \frac{16 - B}{8B}. \tag{13}$$

Applying the mean value equation (12) and remembering that λ is constant, we obtain as our equilibrium condition

$$\oint [G(\mu^2)]^{-1/2} d\mu = [(16 - B)/8B\lambda] \oint (\lambda^2 - \mu^2)[G(\mu^2)]^{-1/2} d\mu. \tag{14}$$

We now come to the consideration of the possible orbits. The type of multiply periodic orbit is determined by the roots of $[F(\lambda)]^{\frac{1}{2}}$ and $[G(\mu^2)]^{\frac{1}{2}}$. The values of these roots are discussed very completely by Pauli. From Eqs. (6) and (8) it is evident that at the libration limits

(where $p_k=0$) the values of these radicals must reduce to zero or in other words the libration limits are given by the real roots of these quantities. Since in our problem λ is constant we need only consider the roots of the biquadratic $[G(\mu^2)]^{\frac{1}{2}}$. For symmetrical orbits it is necessary for the electron to swing between plus and minus values of one root which we call $+(x_1)^{\frac{1}{2}}$ and $-(x_1)^{\frac{1}{2}}$. The other root, x_2 may be shown to be negative giving imaginary positions of the electrons. We may therefore write $[G(\mu^2)]^{\frac{1}{2}}=[(x_1-\mu^2)\ (|x_2|+\mu^2)]^{\frac{1}{2}}$. It is possible by using special values of λ and μ to determine a relation between x_1 and x_2 and λ. This is determined in Pauli's paper and the same relation holds in our problem, that is

$$1-x_1=\frac{(\lambda^2-1)^2(\lambda^2-|x_2|)}{(1-|x_2|)\lambda^2(1+\lambda^2)-(\lambda^2-1)^2|x_2|} \tag{15}$$

and the relations involving B and A are given by

$$A=(1-x_1)(1+|x_2|) \qquad B=2(\lambda^4+x_1|x_2|)/\lambda(1+\lambda^2). \tag{16}$$

From the equilibrium condition of the nucleus (14) we have the equation

$$\begin{aligned}&\mathscr{S}[(x_1-\mu^2)(|x_2|+\mu^2)]^{-1/2}d\mu=\\&\quad[(16-B)/8B\lambda]\mathscr{S}(\lambda^2-\mu^2)[(x_1-\mu^2)(|x^2|+\mu^2)]^{-1/2}d\mu.\end{aligned} \tag{17}$$

The integrals occurring in this equation are elliptic and must be reduced to standard forms before computations may be made. This may be done by the substitution

$$\mu=-(x_1)^{1/2}\cos\phi \quad \text{and} \quad k^2=x_1/(x_1+|x_2|). \tag{18}$$

Using $K(k)$ and $E(k)$ to represent elliptic integrals of the first and second kind respectively, the equilibrium condition then reduces to (See Pauli's paper for details)

$$[(\lambda^2+|x_2|)-8B\lambda/(16-B)]K(k)=(x_1+|x_2|)E(k). \tag{19}$$

A second condition is given by $J_2/J_3=1$ and using (8) we obtain

$$2\pi J_2/J_3=A^{-1/2}\mathscr{S}[(x_1-\mu^2)(|x_2|+\mu^2)]^{1/2}(1-\mu^2)^{-1}d\mu. \tag{20}$$

This may also be reduced to standard forms by the same substitution, giving finally,

$$\begin{aligned}\frac{\pi}{2}\left(\frac{J_2}{J_3}+1\right)&=\frac{(x_1+|x_2|)E(k)-(1-x_1)|x_2|K(k)}{[(1-x_1)(1+|x_2|)(x_1+|x_2|)]^{1/2}}\\&\quad+F(\beta,k')E(k)-[F(\beta,k')-E(\beta,k')]K(k)\end{aligned} \tag{21}$$

where $k'^2=1-k^2$ and $\beta=1-x_1$.

In our problem we must determine the three constants, λ, x_1, and $|x_2|$. We may do this now since we have three equations, (19), (21) and (15), involving only these constants. Since two of these equations are complicated transcendental equations the best method of attack is trial and error. In this case a value of λ was assumed and values of x_1 and $|x_2|$ corresponding to this value were found such that Eqs. (15) and (19) were satisfied. These values were substituted in (21) and a curve plotted for the variation of J_1/J_2 with λ. By interpolation and rechecking, satisfactory values were obtained. They are:

$$\lambda = 1.3753 \qquad x_1 = .83389 \qquad |x_2| = .37839.$$

From these values the nuclear separation and energy may be computed. We have

$$B = 2(\lambda^4 + x_1|x_2|)/\lambda(1+\lambda^2) = 1.9580$$

and

$$A = (1-x_1)\ (1+|x_2|) = .22896$$

and therefore from (7) we obtain

$$c/a_1 = n_3^2 \cdot (B/16A) = .53448.$$

From (9) we obtain

$$W = -(e^2/2c)[(8/B) - 1] = -5.7735\,Rh \tag{22}$$

where R is the Rydberg constant.

We have now computed the energy and constants of the dynamical problem of an electron of two units of charge and of mass moving under the attraction of two fixed nuclei with unit charges. The next part of the problem is to determine the effect of the interaction of the two electrons, which has been neglected in this section.

III. The Energy to a First Approximation

In the preceding section we have neglected the repulsion due to the interaction of the two electrons. When the interaction was neglected the position of the electrons relative to each other was immaterial. Now, however, the relative position is very important and we must assign a position to them. It is assumed that the electrons are always diametrically opposed, that is, they are always 180° apart. From the symmetry of the model this is the only reasonable assumption that can be made.

To compute the interacting effect of the electrons, we turn to perturbation theory. An approximate value of the disturbance due to the electrons can be obtained by applying to the orbit obtained in the last

section, the theorem that the energy of the perturbed orbit is to a first approximation equal to the energy of the unperturbed orbit plus the perturbative potential averaged over the unperturbed orbit.[9] Since the perturbing force amounts to about $\frac{1}{2}$ to $\frac{1}{6}$ of the real force we would not expect this approximation to hold very closely. Our theorem says

$$W = W_0 + \overline{V}_p. \tag{23}$$

In our case the perturbing potential is given by

$$V_p = e^2/2\rho = e^2/2c[(\lambda^2 - 1)(1 - \mu^2)]^{1/2}. \tag{24}$$

To average this over the unperturbed orbit we must use the mean value equation, (12). The denominator then occurring may be integrated by using the same substitution as for Eq. (17). The numerator after substitution consists of an integral involving a sixth power under a radical. The presence of the $(\lambda^2-\mu^2)$ term combined with the radical makes it impossible to reduce the integral to standard elliptic forms by substitutions. The easiest way to integrate this expression is graphically.[10] First, it is necessary to obtain values of the time, t, corresponding to successive values of μ, by integrating the equation for dt used in (12). We obtain after integrating

$$t = \frac{\lambda^2 + |x_2|}{(x_1 + |x_2|)^{1/2}} \int_{\cos^{-1} a x^{-1/2}}^{\pi/2} (1 - k^2 \sin^2 \phi)^{-1/2} d\phi - (x_1 + |x_2|)^{1/2} \int_{\cos^{-1} a x^{-1/2}}^{\pi/2} (1 - k^2 \sin^2 \phi)^{1/2} d\phi$$

or

$$t = \frac{\lambda^2 + |x_2|}{(x_1 + |x_2|)^{1/2}} [\overline{K}(k) - F(k,\phi)] - (x_1 + |x_2|)^{1/2} [E(k) - E(k,\phi)]. \tag{25}$$

We may now plot values of $Q = (1-\mu^2)^{-\frac{1}{2}}$ directly against time. This was done on a large scale and the area measured with a planimeter giving an accuracy of more than one part in one thousand. The graphical integration gives

$$\int_0^{x_1^{\frac{1}{2}}} (1 - \mu^2)^{-1/2} dt = 3.7857. \tag{26}$$

[9] For complete discussion see J. H. Van Vleck, Quantum Principles and Line Spectra, Bulletin N. R. C. No. 48, p. 189 (1926).

[10] It is not advisable to plot the integrand against μ because at the end points the integrand goes to infinity.

The perturbing potential may now be computed

$$\overline{V_p} = \frac{e^2}{2}\frac{\overline{1}}{\rho} = \frac{e^2}{2a_1}\frac{a_1}{c}\frac{3.7857}{(.94417)(2.86737)} = 2.1662Rh. \tag{27}$$

Making use of Eqs. (22), (23) and (27) the energy of the hydrogen molecule may be computed to a first approximation, thus

$$W = (-5.7735 + 2.6162)Rh = -3.1573Rh. \tag{28}$$

IV. Application of Kramers' Method to the Hydrogen Molecule

The approximation used in the preceding section is not sufficient for our purpose because the perturbing force is such a large fraction of the actual force. In the crossed-orbit helium problem the same difficulty is present with this first approximation since in that case the perturbing force at its maximum value amounts to 50% of the actual force. In order to decrease the ratio of these forces Kramers tries other methods. One method is to use $(Z-\alpha)$ as the nuclear charge in the unperturbed orbit and then balance this by considering $-\alpha e^2/r+e^2/4\rho$ as the perturbing potential. In this case r is the distance of the electron from the nucleus and α is suitably chosen to reduce the ratio of the forces as much as possible. These values must be multiplied by two for both electrons giving $e^2/2\rho$ as the interaction term of the electrons. Kramers finds however that, for helium, the ratio of the forces, under these potentials, is not materially reduced. He does find, though, that if he considers the electron to be under the influence of a potential of the form $-(Z-\alpha)e^2/r+C/\rho^2$ with a perturbing potential of the form $-\alpha e^2/r-C/\rho^2+e^2/4\rho$, the ratio of the perturbing to the real force is greatly reduced. This method is especially advantageous in Kramers' problem because the motion under this new unperturbed potential is almost as simple as without the second term. The influence of this term is merely to decrease the angular velocity of the electron about the nucleus in a given ratio. The only change necessary in the equations of motion is that we replace p_ϕ by p_ϕ' keeping, however, as the quantum condition $p_\phi = h/2\pi$ for the two electrons.

Kramers' method of reducing the ratio of the perturbing to the real force can also be used advantageously for the computations on the crossed-orbit model of the hydrogen molecule. This may be easily seen from a consideration of the Hamiltonian function. In place of the original Hamiltonian function given by (5) we shall have (remem-

bering $p_\lambda = 0$) as the Hamiltonian function of the new unperturbed orbit

$$H_0 = \frac{1}{4c^2 m(\lambda^2 - \mu^2)}\left[(1-\mu^2)p_\mu^2 + \left(\frac{1}{(\lambda^2-1)} + \frac{1}{1-\mu^2}\right)p_\phi'^2\right] - \frac{4Z'e^2}{c}\frac{\lambda}{(\lambda^2-\mu^2)} + \frac{Z^2e^2}{2c} = W_0 \tag{29}$$

where $Z' = (Z-\alpha)$ and $p_\phi'^2 = p_\phi^2 + 4m\beta e^2$. For the perturbing potential we shall have

$$\Delta E = -\frac{4\alpha e^2}{c}\frac{\lambda}{(\lambda^2-\mu^2)} - \frac{\beta e^2}{c^2(\lambda^2-1)(1-\mu^2)} + \frac{e^2}{2c[(\lambda^2-1)(1-\mu^2)]^{\frac{1}{2}}}. \tag{30}$$

This perturbing potential just balances the changes in the unperturbed orbit and includes the interaction term. Perhaps the nature of the perturbing potential will look more familiar in other coordinates. It becomes

$$\Delta E = -\frac{2\alpha e^2}{r_1} - \frac{2\alpha e^2}{r_2} - \frac{\beta e^2}{\rho^2} + \frac{e^2}{2\rho} \tag{31}$$

where r_1, r_2 and ρ have the meaning given in Eq. (1). To apply this to a given problem α and β must be chosen so as to reduce the square of the ratio of the perturbing to the real force as much as possible.

The changes which occur in the original perturbed orbit due to the presence of the α and β terms in the new unperturbed motions may easily be given a physical interpretation. The introduction of $(Z-\alpha)$ changes the nuclear attraction. The replacement of the angular momentum p_ϕ by the new value p_ϕ' has the effect of decreasing the velocity of rotation by a given amount so that the repelling force of the electron is just balanced by the decrease in the centrifugal force. This method is not quite as simple to use in the case of the hydrogen molecule as it was in Kramers' case of the helium atom. In Kramers' case it was easy to derive an expression for the quantized energy of the new unperturbed motion in terms of the old motion. In this case it is necessary to obtain the energy of the unperturbed motion in the same tedious manner as was used in the original motion.

In order to apply the theorem relating to the average value of the perturbative potential accurately it is necessary that the time average of the square of the ratio of the perturbing to the real force be made as

small as possible. We use the relation $F=-\text{grad}\,(\Delta E)$ and obtain the result

$$M^2=(\text{grad}\,\Delta E)^2/(\text{Real Force})^2=Z^{-2}\{\alpha^2-\mathcal{A}\alpha+\mathcal{B}\gamma^2-\mathcal{C}\gamma+\mathcal{D}\alpha\gamma+\mathcal{E}\} \tag{32}$$

where $\gamma=\beta/c$ and

$$\mathcal{A}=\frac{\lambda(\lambda^2-\mu^2)(\lambda^2+3\mu^2)(1-\mu^2)^{1/2}}{4(\lambda^2-1)^{\frac{1}{2}}(1+3\lambda^2)(1-\mu^2)(b+\mu^2)}$$

$$\mathcal{B}=\frac{(\lambda^2-\mu^2)^4}{4(\lambda^2-1)^3(1+3\lambda^2)(1-\mu^2)^3(b+\mu^2)}$$

$$\mathcal{C}=\frac{(\lambda^2-\mu^2)^4(1-\mu^2)^{1/2}}{8(\lambda^2-1)^{5/2}(1+3\lambda^2)(1-\mu^2)^3(b+\mu^2)}$$

$$\mathcal{D}=\frac{\lambda(\lambda^2-\mu^2)(\lambda^2+3\mu^2)}{(\lambda^2-1)(1+3\lambda^2)(1-\mu^2)(b+\mu^2)}$$

$$\mathcal{E}=\frac{(\lambda^2-\mu^2)^4}{64(\lambda^2-1)^2(1+3\lambda^2)(1-\mu^2)^2(b+\mu^2)}.$$

In the above relations b has been written for $\lambda^2(\lambda^2-1)/(1+3\lambda^2)$.

It is now necessary to average each of the coefficients over the unperturbed orbit. To do this we substitute back in the mean value Eq. (12). The integrals arising from this substitution are very complicated and only some of them may be reduced to standard elliptic forms. The coefficients of α and γ after substitution in (12) consist of a sixth power under a radical similar to the numerator in (24) and one must resort to graphical integration. The integrals were all evaluated graphically and, where possible, the actual integration was also carried out. In the latter cases, the integrations all agreed closer than one part in one thousand. The graphical integration was carried out in the same manner as described for Eq. (24). After integration, Eq. (32) becomes:

$$M^2=Z^{-2}\{\alpha^2-.60205\alpha+3.2218\gamma^2-1.0673\gamma+3.2714\alpha\gamma+.09844\} \tag{33}$$

This expression is a minimum when $\alpha=.17750$ and $\gamma=.07551$. Substituting these back into M^2 and letting $Z=1$ we find $M^2=.00475$ which shows that we have reduced the time average of the square of the ratio of the perturbing to the real force to less than one part in 200. Also in the above equation if we take $\beta=0$, then α becomes .30103 which gives .00783 as a minimum value of M^2. We shall make calcu-

lations with each of these sets of coefficients and they should check within one part in one hundred. We now have the perturbation constants and are ready to compute the energy of the new unperturbed motion and the average perturbative potential.

In order to find the method which would work most accurately for the crossed-orbit model of the hydrogen molecule, preliminary computations were made using the Bohr circle model as an example. This model has the advantage that it may be easily solved accurately and the energy is known when the interaction of the electrons is included. The problem was to apply Kramers' method to this simple case and find the manner in which it applied most accurately. The different ways in which it was applied consisted in assuming different charges on the nuclei for different portions of the energy, in each case balancing them by means of the perturbative potential in such a manner that the final charge in each case would be Z alone. An example would be to consider the charge on the nuclei to be $(Z-\alpha)$ both for the equilibrium of the nuclei and for the equilibrium of the electrons. In this case a term $(2Z\alpha-\alpha^2)/2c$ must be included in the perturbative potential so that the final mutual potential energy of the nuclei is $Z^2e^2/2c$. However, it was found that for this simple case, an exact solution could be obtained when the nuclei were considered in equilibrium under the charge Z and the electrons were in equilibrium under the charge $(Z-\alpha)$. An exact solution is obtained because it is possible to reduce the ratio of the perturbing to the real force to zero.

Coming back to the crossed-orbit model, our new unperturbed motion has for its Hamiltonian function

$$H_0 = \frac{1}{4c^2m(\lambda^2-\mu^2)}\left[(1-\mu^2)p_\mu^2 + \left(\frac{1}{\lambda^2-1}+\frac{1}{1-\mu^2}\right)p_\phi'^2\right] - \frac{4Z'e^2}{c}\frac{\lambda}{(\lambda^2-\mu^2)} + \frac{Z^2e^2}{2c} \tag{34}$$

where

$$p_\phi'^2 = p_\phi^2 + 4m\beta e^2 \qquad \text{and} \qquad Z' = Z - \alpha \tag{35}$$

In this case also we will consider the charge on the nucleus as Z when we are considering the equilibrium of the nuclei and as $(Z-\alpha)$ when we are considering the equilibrium of the electrons. We shall quantize the real angular momentum p_ϕ and not p_ϕ' which is the angular momentum of the false unperturbed orbit which we have set up. We may consider p_ϕ' as quantized directly if we use a false quantum

number n_3'. The value of this false quantum number may be determined from (35), since $\beta=\gamma c$ thus,

$$n_3'^2 = n_3^2 + (16m\gamma e^2 c\pi^2)/h^2 = n_3^2 + (4c\gamma/a_1) \tag{36}$$

where the radius of the one-quantum orbit of the hydrogen atom is given by $a_1=h^2/4\pi^2me^2$.

Using (7) we obtain for the new unperturbed motion

$$c/a_1 = n_3'^2\,[B/16A(Z-\alpha)] \tag{37}$$

The factor $(Z-\alpha)$ enters since this relation really comes from the equilibrium of the electrons. Replacing (37) in (36) we obtain

$$n_3'^2 = n_3^2 + [4\gamma n_3'^2 B/16A(Z-\alpha)] = n_3^2 + .19635n_3'^2$$

in which the values of A and B are those given in (22) and the values of α and γ are those given in (33). This equation may now be solved for n_3' where $n_3=1$, we obtain $n_3'=1.1155$ and $J_2/J_3=.89647$.

Since, for the condition of equilibrium of the nuclei, the charge of $Z=1$ is used on each nucleus, the Eq. (19) remains the same. Eq. (15), which involves only the roots of $G(\mu^2)$, clearly, will not change. Therefore to obtain the new values of λ, x_1 and $|x_2|$ we must again solve Eqs. (19), (21) and (15) with the single exception that J_2/J_3 is equal to .89647 instead of unity. This computation is not as difficult as the first since the curve between J_2/J_3 has already been plotted. The final values are obtained by trial and error as before. The new values are

$$\lambda = 1.4026 \qquad x_1 = .81160 \qquad |x_2| = .39852 \tag{38}$$

from which $B=2.0152$ and $A=.26348$. The nuclear separation $2c$ is given by $2c/a_1=1.4460$ and the energy of our new unperturbed orbit is given by

$$W_0 = -\frac{e^2}{2c}\left[\frac{8(Z-\alpha)}{B} - 1\right] = -3.1339\,Rh. \tag{39}$$

It is now necessary to average the perturbative potential over this new unperturbed orbit. The perturbing potential as given in (30) becomes

$$\overline{\Delta E} = -\frac{4\alpha e^2\lambda}{c}\overline{(\lambda^2-\mu^2)^{-1}} - \frac{\beta e^2}{c^2}\overline{[(\lambda^2-1)(1-\mu^2)]^{-1}} + \frac{e^2}{2c}\overline{[(\lambda^2-1)(1-\mu^2)]^{-1/2}} \tag{40}$$

The average values are obtained by substitution in the time average Eq. (12).

By reducing the integrals, then occurring, to standard elliptic integrals of the 1st, 2nd and 3rd kind, we obtain as the average of the perturbative potential over the new unperturbed orbit

$$\overline{\Delta E} = [-1.7017 - .4017 + 1.8403]Rh = -.2631Rh. \quad (41)$$

The final value of the energy may now be computed. We obtain for this, combining (39) and (41)

$$W = W_0 + \overline{\Delta E} = [-3.1339 - .2631]Rh = -3.397Rh$$
$$= 45.2 \text{ volts}. \quad (42)$$

In order to furnish a check on this value of the energy we may next compute the energy and dimensions with the other set of constants $\beta = 0$ and $\alpha = .30103$. In this computation n_3 is not changed. This means that the relative dimensions of the model are not changed but only the absolute values. Repeating the same steps as before we obtain as the final value of the energy

$$W = W_0 + \overline{\Delta E} = [-2.4274 - .9945]Rh = -3.4219Rh.$$

This value agrees with the value of the energy given in (42) as well as could be expected with the approximation used in this case (see Eq. 33) and it verifies the latter parts of the previous calculations.

V. Comparison with Experiment and Conclusions

An experimental value of the energy of the hydrogen molecule may be determined from the heat of dissociation and the energy of two hydrogen atoms. The most recent determination is that of Witmer,[11] who obtained the heat of dissociation from spectral data. His most probable value is 4.34 volts or 100,100 cal/mol. This result is higher than the previous result of Langmuir,[12] who obtained 3.6 volts or 84,000 cal/mol., but it agrees with the earlier values of Isnardi[13] and Wohl.[14] Witmer's value corresponds to $(2\times13.54+4.34)$ 31.42 volts for the hydrogen molecule. The energy given above of 45.2 volts for the crossed orbit model is so much higher than experiment that the model cannot correspond with reality. This result is not very surprising since

[11] E. E. Witmer, Proc. Nat. Acad. Sci. **12**, 238 (1926).
[12] I. Langmuir, J. Amer. Chem. Soc. **37**, 417 (1915).
[13] T. Isnardi, Zeits. f. Elektrochem. **21**, 405 (1915).
[14] K. Wohl, Zeits. f. Elektrochem. **30**, 49 (1924).

the three body problems of the neutral helium atom and the hydrogen molecule ion do not agree with experiment. Furthermore the moment of inertia deduced from this model is 4.91×10^{41} gm cm, which is much larger than the value derived from specific heat data. This is another example of the deficiency of the older or classical quantum theory. It is hoped that the new matrix theory, which has been introduced since this work was started, will clear up the quantum theory problem of more than two bodies.*

The writer wishes to express his sincere appreciation to Professor J. H. Van Vleck for his interest and assistance throughout this work.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF MINNESOTA,
August 15, 1926.

* Note added in Proof: Since the above was written a paper has come out by Alexandrov in Ann. der Physik **81,** 603, (1926) treating the problem of the hydrogen molecule ion from the standpoint of the new wave mechanics. This paper indicates that the new mechanics gives a value of the energy in agreement with experiment.

THE ELECTRON AFFINITY OF HYDROGEN AND THE SECOND IONIZATION POTENTIAL OF LITHIUM

By Linus Pauling[1]

Abstract

On the assumptions that electrons in atoms and ions can be considered to be in hydrogen-like orbits under the influence of an effective nuclear charge $(Z-s)e$, and that the screening constant s is the same for ions with the same structure, there is calculated for the second ionization potential of lithium the value 76.2 v., and for the electron affinity of hydrogen atoms the value −1.85 k. cal./mol. These values are shown to lie within the range permitted by existing spectral and thermochemical data. With the use of the electron affinity of hydrogen it is shown that theoretically the hydride ion should be unstable in aqueous solution.

Introduction

The electron affinity of hydrogen. Two recent attempts have been made to determine the electron affinity of hydrogen, E_H; i. e., the amount of energy evolved by the reaction

$$H + E^- = H^-.$$

In both cases use is made of thermochemical data; thus if all quantities but E_H are known, the following equation suffices for its determination:

$$E_H - D_H = Q_{MH} + S_M + I_M - U_{MH}.$$

Here D_H is the heat of dissociation of $\frac{1}{2}H_2$ to H, Q_{MH} is the heat of formation of crystalline MH from metallic M and $\frac{1}{2}H_2$, S_M is the molal heat of sublimation of M at low temperatures, I_M is the work of ionization of M, and U_{MH} is the molal crystal energy of MH. With the exception of U_{MH} the required energy quantities are known with considerable accuracy. The crystal energy may be calculated by the Born equations; for the sodium chloride structure, for example, we have

$$U_{MX} = 614 \cdot (1 - 1/n)(\rho/M)^{1/3},$$

in which ρ is the density, M the molecular weight (per MX), and n the repulsion exponent of the crystal. The value of n is in general found from the compressiblity of the crystal; in the absence of any data for metal hydrides, however, n must be estimated, and the dis-

[1] Fellow of the John Simon Guggenheim Memorial Foundation.

crepant results of different workers arise from variations in its estimated value.

Joos and Hüttig[2] contend that the replacement of another alkali metal ion by lithium ion should cause the same change in n as the replacement of a halogen ion by the hydride ion, H^-; for in each case an ion whose outer shell contains eight electrons is replaced by one whose outer shell contains only two electrons. On using the corresponding value

$$n_{MH} \cong n_{LiX} \cong 6,$$

they obtain, with the use of data from sodium, potassium, rubidium, and caesium hydrides, the average result $E_H - D_H = -10$ k. cal./mol, which gives $E_H = 23$ k. cal./mol if D_H is taken as 33 k. cal./mol, or

$$E_H = 30 \text{ k.cal./mol} \qquad (1)$$

if D_H is given the more generally accepted value 40 k. cal./mol.[3]

Kasarnowsky[4] has criticized this procedure, and adopted another one. He states that the values of U for the lithium salts calculated by substituting $n=6$ in the Born formula, as was done by Joos and Hüttig, are in considerable disagreement with the experimental values of that quantity, and concludes that this procedure should not be followed. Finding that in general U for a lithium salt is experimentally approximately equal to U for another alkali halide of the same structure and same molecular volume, he makes the assumption that this is true also for the alkali hydrides. From data for lithium, calcium, and barium hydrides, LiH, CaH_2, and BaH_2, chosen because of their relatively accurately known densities, he obtains (assuming calcium and barium hydrides to have the calcium fluoride structure) the value $-62+4$ k. cal./mol for $E_H - D_H$. The concordant value -59 k. cal./mol is obtained from sodium hydride, NaH, with the use of an estimated molecular volume. With $D_H = 40$ k. cal./mol, this gives

$$E_H = -22 \text{ k. cal./mol.} \qquad (2)$$

Kasarnowsky states that the error in his calculations can hardly exceed ± 20 k. cal./mol, and that the electron affinity of hydrogen must hence be negative.

[2] G. Joos and G. Hüttig, Zeits. f. Elektrochem. **32**, 201 (1926); **32**, 294 (1926).

[3] The value $E_H = 37$ k. cal./mol was similarly obtained in an earlier computation, a slightly different value of n being used. See K. Fajans, Zeits. f. Elektrochem. **26**, 493 (1920).

[4] J. Kasarnowsky, Zeits. f. Physik **38**, 12 (1926). See also Joos and Hüttig, ibid., **39**, 473 (1926).

In order to substantiate this very interesting result it is desirable to have an independent determination of the energy quantity E_H. This is especially true in view of the great uncertainty inherent in calculations of the crystal energies of hydrides. In both previous attempts it is assumed that the crystal energy of a hydride can be taken as equal to that of a lithium salt with the same molecular volume; the disagreement in results arising in a difference in the method of determining the crystal energies of the lithium salts, and in the choice of experimental data. It seems highly probable, however, that this fundamental assumption is in error. The repulsion exponent (i. e., the compressibility) of a salt containing the lithium ion, with two electrons contained within a radius of about 0.40A, would hardly be expected to be the same as that of a salt containing the hydride ion, with two electrons within the very large radius of about 1.5A.[5] The hydride ion has far the most open structure of all known atoms and ions; and it is to be expected that this structure will have an appreciable influence on the repulsion exponent of hydride crystals.

The second ionization potential of lithium. The second ionization potential of lithium, the amount of work required in order to remove one further electron from the singly ionized lithium atom, Li^+, in the normal state $1S$, has not been directly determined by the method of electron impact; nor has the term value $1S$ been found from the analysis of the lithium spark spectrum. Schüler[6] has recently evaluated sixteen terms of par-lithium II, including $4S$, $5S$, $6S$, and $7S$. From a comparison of the values of the effective quantum number of these terms of lithium II with those of helium, he has, by a rather violent extrapolation, estimated for $1S$ the term value 648000 ± 32000 cm^{-1}, corresponding to a second ionization potential for lithium of between 76 and 84 v. Werner[7] has similarly obtained fifteen term values of par-lithium II, including $3S$, $4S$, and $5S$; his values and Schüler's being in good agreement. He likewise extrapolates to $1S$, for which he estimates the effective quantum number to lie between 0.85 and 0.90. This corresponds to a term value between 541000 and 606000 cm^{-1}, and a second ionization potential of lithium between 66.9 and 74.9 v.

It is evident that from spectroscopic data now available it can be concluded only that the second ionization potential of lithium is probably in the range between 67 and 84 v.*

[5] See Note 9.
[6] H. Schüler, Zeits. f. Physik **37**, 568 (1926).
[7] S. Werner, Nature **118**, 154 (1926).
*See Note, p. 291.

The Energy of Helium-like Ions

Since the early days of the quantum theory of spectra the x-ray term values have been explained by the assumption that the electron orbits are hydrogen-like, the nuclear charge Ze being diminished through the mutual screening effect of the electrons to the effective value $(Z-s)e$, in which s is called the screening constant.[8] In ions with the same number of electrons and of similar structure, but with different atomic numbers, s is assumed constant. In the course of the application of this method of treatment to the polarizabilities, diamagnetic susceptibilities, and sizes of ions with rare gas structures, it was observed that it also allows the prediction of the energies of ions with the helium structure.

The energy of a hydrogen-like electron characterized by the total quantum number n and under the influence of the effective nuclear charge $Z_{eff}.e$ is

$$-2\pi^2 me^4 Z^2_{eff}/h^2n^2 = -13.54\, Z^2_{eff}/n^2 \text{ volts}.$$

In helium there are two equivalent electrons, each with $n=1$; the total energy of a helium-like atom or ion is, then,

$$W = -27.08(Z-s)^2 \text{ volts}. \tag{3}$$

Let us represent by I_1 and I_2 the work required to remove to infinity the first and the second electron, respectively. The removal of the first electron leaves the second under the influence of the entire nuclear charge Ze, and in the lowest orbit, with $n=1$; we accordingly have

$$I_2 = 13.54\, Z^2 \text{ volts}. \tag{4}$$

Since $I_1+I_2=-W$, the ionization potential I_1 is given by the equation

$$I_1 = 27.08(Z-s)^2 - 13.54\, Z^2 \text{ volts}. \tag{5}$$

The experimental value of I_1 for helium is 24.5 v., so that $W=78.7$ v. and $Z-s=1.705$. Assuming that this value of $s=0.295$ holds also for H^-, Li^+, etc., the predicted energy values given in Table I are obtained. It is believed that these values are very close to the true ones; for the consideration of the more complicated problem of the term values of the K-level in heavier elements has shown that s undergoes only a slight change from element to element.

The value 76.2 v. for the second ionization potential of lithium is almost exactly in the middle of the entire range of probable values

[8] See, for example, A. Sommerfeld, "Atombau," 4th Ed., pp. 454–461 and 546–551.

given by Schüler and Werner. Corresponding to it is the predicted term value 618000 cm^{-1} for $1S$ of lithium II. In addition the interpolated value 118700 cm^{-1} for $2S$ of lithium II may confidently be predicted; this does not differ greatly from Werner's extrapolated

TABLE I

	$Z-s$	$-W$	I_2	I_1
H^-	0.705	13.46 v.	13.54 v.	−0.08 v.
He	1.705	78.7	54.16	+24.5
Li^+	2.705	198.1	121.86	76.2
Be^{++}	3.705	372	217	155
B^{+++}	4.705	600	338	262

value 120000 cm^{-1}. The predicted values for these terms may be useful in the identification of observed lines in the lithium spark spectrum. No comparison with experiment can be made for Be^{++}, B^{+++}, etc.

The most interesting result of this calculation is the value of I_1 for H^-, which is the electron affinity of hydrogen. Converting it into k. cal./mol, we obtain

$$E_H = -1.85 \text{ k.cal./mol} \tag{6}$$

As the discussion in the introduction has shown, this is not in disagreement with the thermochemical data. Kasarnowsky's statement that the electron affinity of hydrogen atoms is negative is substantiated; but its value is much nearer zero than Kasarnowsky's values.[9]

The stability of the hydride ion in solution. As mentioned by Kasarnowsky, the negative value of the electron affinity of hydrogen illustrates well the part played in chemical reactions by crystal energy; for in hydride formation the crystal energy in effect not only dissociates the hydrogen molecules, volatilizes the metal, and ionizes its

[9] The treatment of orbits as hydrogen-like permits the theoretical prediction of atomic radii, in order of magnitude at least. In the absence of a completely rational procedure, we may assume the atomic radius to be approximately equal to the distance from the nucleus at which the characteristic functions corresponding in the wave mechanics of Schrödinger to the hydrogen-like "orbits" in the atom become nearly zero. Schrödinger (Ann. d. Physik **79**, 371 (1926)) has remarked that this distance is approximately equal to the major axis of the corresponding ellipse. We may then write

$$r = r_0 \cdot n^2/Z_{\text{eff}} = 1.064\, n^2/Z_{\text{eff}} \text{ Angstroms}$$

Using the values of $Z_{\text{eff.}} = Z-s$ given in Table I, we obtain

	H^-	He	Li^+	Be^{++}	B^{+++}
$r=$	1.510	0.625	0.394	0.287	0.226A.

These values are in reasonable agreement with the Li^+-H^- distance in crystalline lithium hydride, 2.05A. (J. Bijvoet and A. Karssen, Proc. Amsterdam Acad; **25**, 27 (1922)), and the less easily interpretable gas-kinetic radius of helium, 0.94A. (K. F. Herzfeld, Handbuch der Physik, Vol. 22, p. 436, (1926).

atoms, but also does work in forming the unstable hydride ion from the atom and electron. In solution in a fused salt also the hydride ion might be stable, for the electrostatic energy against the surrounding oppositely charged ions would take the place of the crystal energy. The value found for the electron affinity of hydrogen shows, on the other hand, that the hydride ion in solution in water would react with the water molecules to form hydroxyl ions and gaseous hydrogen. To illustrate the use of the electron affinity in thermochemical calculations this instability in solution will be considered in detail.

The reaction of a univalent ion X^-_{Sol} in solution and a water molecule to form hydroxyl ion and HX may be written as follows:

$$\begin{array}{rl}
X^-_{Sol} \rightarrow X^-_{Gas} & -W_{X^-} \\
X^-_{Gas} \rightarrow X + E^- & -E_X \\
H_2O \rightarrow H^+_{Sol} + OH^-_{Sol} & -Q_{H_2O} \\
H^+_{Sol} \rightarrow H^+_{Gas} & -W_{H^+} \\
H^+_{Gas} + E^- \rightarrow H & +E_{H^+} \\
H + X \rightarrow HX & +D_{HX} \\
\hline
X^-_{Sol} + H_2O \rightarrow OH^-_{Sol} + HX & +Q\ ,
\end{array} \tag{7}$$

with

$$Q = D_{HX} + E_{H^+} - W_{H^+} - Q_{H_2O} - E_X - W_{X^-}. \tag{8}$$

Here W_{X^-} and W_{H^+} are the heats of hydration of the ions X^- and H^+; the significance of the other symbols is evident from their use. Of the energy quantities entering into Q, E_{H^+} is equal to 13.54 v., or 311 k. cal./mol; W_{H^+} to 249.6 k. cal./mol[10]; and Q_{H_2O} to 13.5 k. cal./mol; so that we have

$$Q = 47.9 + D_{HX} - W_{X^-} - E_X\ . \tag{9}$$

The values of Q for the hydride ion and the halide ions are given[11] in Table II.

TABLE II

	D_{HX}	W_{X^-}	E_X	Q
H^-	80	87*	− 1.87	42.8 k. cal./mol
F^-	78.5 $+D_F$	87.0	64$+D_F$	−26.6
Cl^-	89	70.1	88	−21.2
Br^-	75	66.2	80	−23.3
I^-	59	61.0	71	−25.1

*Assuming the radii of hydride and fluoride ions to be equal.

The entropy change during the reaction of Eq. (7) may be neglected, on account of the similarity of the original and final substances;

[10] The heats of hydration are taken as the free energies of hydration given by T. J. Webb, Proc. Nat. Acad. Sci. **12**, 524 (1926); the difference between energy and free energy is not great enough to matter in this calculation.

[11] D_{HX} from H. Senftleben and I. Rehren, Zeits. f. Physik **37**, 529 (1926); W_{X^-} from Webb; E_X from E. v. Angerer and A. Müller, Phys. Zeits. **26**, 643 (1925).

hence Q may be identified with the free energy change $-\Delta F = RT\ln K$, in which K is the equilibrium constant of the reaction. The large negative values of Q for the halide ions show that the ions are stable in solution, and do not hydrolyse. On the other hand, the large positive value for the hydride ion requires that it be unstable in solution; thus it is in equilibrium with 1 mol/liter of hydroxyl ion and with hydrogen at one atmosphere pressure only at a concentration of about 10^{-29} mol/liter.

MUNICH, OCTOBER 9, 1926.

Note added to proof. It is necessary to mention, moreover, that the new quantum mechanics leads to the result that the normal state of helium is not an extrapolation of the S series of orthohelium, but lies between the ortho-and parhelium series. See Heisenberg, Zeits. f. Physik. **39**, 499 (1926).

MEASUREMENT OF INDEX OF REFRACTION OF GASES AT HIGHER TEMPERATURES

By E. W. Cheney

Abstract

The thermal coefficients of the indices of refraction of air, N_2, SO_2, NH_3, and CO_2.—For light of the visible spectrum these coefficients were not found to differ from the thermal coefficients of density change in the range 0–300°C. At 0°C, 760 mm the values of $(n-1)\ 10^7$ for λ5852A, 6143A, and 6678A were found to be:

λ	Air	N_2	NH_3	CO_2	SO_2
5852A	2925	2985	3795	4485	6637
6143A	2919	2977	3785	4473	6615
6678A	2912	2969	3771	4465	6598

Incidentally the *rate of expansion of quartz with temperature* was found to be constant within the temperature interval 25–300°C, and to have an average value of expansion coefficient of $0.946(10)^{-6}$. A *kilowatt neon Geissler tube* is described.

A FABRY-PEROT interferometer was used to measure at higher than room temperatures the indices of refraction of several gases including some having polar molecules. It was hoped at the beginning of the experimental work that time would be had to extend the measurements into the infra-red. A recent article[1] gives very well the theory of the instrument and methods of use.

Apparatus. Fig. 1 will give an idea of the present experimental arrangement. It shows the optical system and an electric furnace encircling the Fabry-Perot interferometer. Light from a neon tube produced Haidinger interference fringes on the slit of the spectroscope. A camera photographed the fringes.

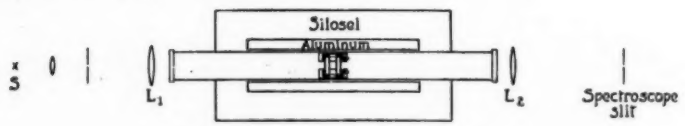

Fig. 1. Arrangement of apparatus.

The neon tube was constructed in the laboratory and furnished a particularly brilliant and satisfactory source for the interference work. The hard glass tube has large cylindrical electrodes, a narrow capillary about five inches long, and contains neon at a pressure of about 5 mm. The tube rests at two points in a water tank. (See Fig. 2.)

[1] W. H. J. Childs, J. Scientific Instruments **3**, Nos. 4 and 5 (1926).

Rubber tubing containing mercury makes the requisite flexible and water-tight seals around the lead-in wires. The tube has operated continuously for hours, with an input of a kilowatt furnished by a 10,000-v., 3-kw transformer.

The circular interferometer mirrors were made by sputtering platinum over their central portions in order to have inert surfaces. They remained good after heating in the furnace provided the glass had been baked for some hours before the sputtering. The laboratory mechanician ground on a lathe three fused quartz posts, (from the Hanovia Chemical Co.) for the etalon. For the more accurate adjustment of lengths, I ground the posts by hand on a flat steel disc. For testing the lengths of the posts one of the interferometer mirrors was mounted

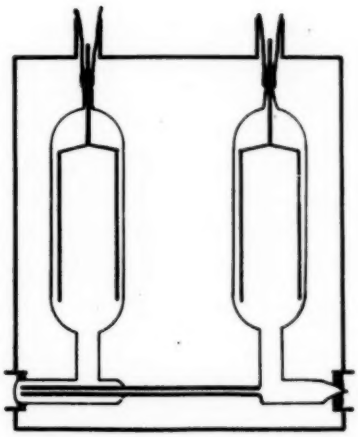

Fig. 2. The neon tube.

horizontally in a converging beam of mercury green light. The three quartz posts stood on this mirror. The second mirror, mounted in a light frame with levelling screws, rested on the quartz posts. By moving the top mirror a little with one or another of the levelling screws until the interference fringes appeared, it was easy to tell which quartz posts were longer. I ground the posts by hand until the Haidinger fringes showed the same order of interference over the whole of the mirrors when they were separated by the quartz posts. The mirrors and posts were then mounted in a steel cylinder about three inches long. Small coiled tungsten springs held the mirrors against the quartz posts. Steel springs were not satisfactory at higher temperatures, owing to variation in elasticity. The interferometer after adjustment was shoved to the center of a steel tube 35 inches long.

An electric furnace with a heating coil wound on a heavy cast aluminum cylinder to give uniform heat distribution surrounded 19 inches of the 35 inch steel tubing, which passed axially through the furnace. A can of Silosel insulated the furnace. This was mounted in a tank of water so that its heat capacity would reduce random temperature fluctuations. The water tank was mounted on screws so that the interferometer could be moved to bring the interference fringes accurately on the slit. Storage cells furnished the heating current and iron wire ballast lamps, kindly donated by the Edison Lamp Works of the General Electric Company, satisfactorily compensated for fall in voltage of the storage cells during long heating periods. With this arrangement the temperature in the furnace would remain constant to within 1/30 of a degree for hours. Changes in temperature of the interferometer due to the heat transference by the gases upon their entrance to the tube, however, caused trouble.

A copper-constantan thermocouple sealed in a glass tube projected through the casing of the interferometer until it was in the space between the interferometer plates. The thermocouple was heated for 50 hours at about 300°C, and then calibrated. A second calibration after 50 hours more of heating showed no change in the thermocouple. A potentiometer and a mirror galvanometer gave the electromotive force and could exhibit a change of 1/30°C in the temperature of the thermocouple. A Weston cell in a constant temperature bath served as a standard e.m.f.

Mercury in an inch bore manometer tube measured the gas pressure. Both surfaces of mercury could be raised and lowered simultaneously to prevent errors due to adhesion. A cathetometer which had been compared with a standard meter bar gave the heights of the mercury column and the readings were properly reduced to standard conditions.

A high grade photographic objective focussed the interference fringes upon the slit of the spectroscope. The rings were photographed on panchromatic plates and were measured with a traveling microscope reading to 1μ. The fractional order of interference at the center of the interference circles is equal to Ad^2-p, where d is the diameter of the p'th ring from the center, and A is a constant for any one wave-length, i.e. $P/(d^2_{p-1}-d^2_p)$, where P is the order of interference. A is determined from measurements on two ring diameters and an approximate value of P. The A's are inversely proportional to the wave-lengths, so that A's measured for different lengths may be reduced to the A for some particular wave-length. This was done for measurements made on many lines and the values averaged, to give as good values for the

various constants as could be obtained with more effort from the usual formula involving the focal length of the projecting lens. The fractional order of interference at the center of the interference circles was determined to the third decimal place.

Preparation of gases. N_2 came from a commercial cylinder and passed over hot copper for elimination of oxygen. The air and N_2 filtered through six feet of drying tubes containing $CaCl_2$ and P_2O_5 and further passed through a liquid air trap on their way to the apparatus.

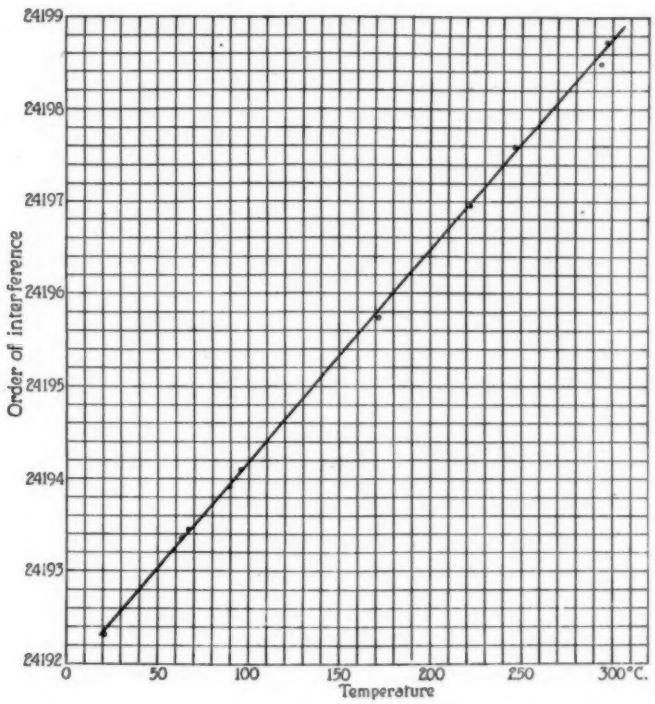

Fig. 3. The variation of the order of interference for vacuum with temperature.

HCl and marble in a Kipp generator furnished CO_2. This was dried by $CaCl_2$ and P_2O_5 and frozen in a liquid air trap. The middle portion of the sublimate was used each time.

The NH_3 came from a tank as a liquid. It boiled out of a Dewar flask equipped with an electric heating coil, and after passing over KOH, froze in the liquid air trap. The middle portion of the distillate was used.

The SO_2 came from a tank, was dried by passage through the drying tubes, and further purified by the usual freezing process.

Measurements. The index of refraction of a gas is given by dividing the order of interference with the gas between the plates by the order of interference with the interferometer evacuated. For the best results the pictures enabling these orders to be computed should be taken at precisely the same temperature. Unfortunately cooling by the admission of the gases made this procedure impossible. Although alterations in the interferometer with change in temperature were not quite continuous, the order of interference for the vacuum, at the same temperature as the gas under consideration, was obtained by interpolation from vacuum values at neighboring temperatures.

Fig. 3 shows the order of interference for a vacuum between the interferometer plates plotted against temperature. The order of interference at the lowest temperature plotted (21.4°C) is 24192.312.

TABLE I

Measured values of $(n-1)\times10^6$ for various gases
Wave-length of light 5852Å. Values reduced to 760 mm pressure

Temp. °K	$(n-1)\times10^6$	Temp. °K	$(n-1)\times10^6$
	Air		
294.5	270	445.1	180
338.3	236	508.1	153
363.1	221	567.5	148
	Nitrogen		
244.5	276	446.1	185
338.7	239	497.0	157
365.6	222	569.3	144
	Ammonia		
294.3	358	445.8	231
339.2	302	499.2	210
366.2	280	568.1	182
	Carbon dioxide		
294.4	411	439.4	277
333.7	373	483.6	247
363.5	334	567.6	222
	Sulfur dioxide		
294.3	612	434.4	418
335.1	537	481.2	371
360.1	499		

The expansion of the interferometer is shown to be moderately uniform. The slope of the line divided by the total order of interference, in Fig. 3, incidentally gives the average coefficient of expansion of quartz as 0.946×10^{-6} for the temperature interval 25°C–300°C, a figure higher than given in the tables. An attempt was made to account for the divergence of this value with Randall's measurements[2]

[2] Randall, Phys. Rev. 30, 216 (1910).

on the thermal coefficient of expansion of quartz by taking account of change in length of the quartz posts due to change in tension of the tungsten springs. The required change in tension did not appear to be of a possible order of magnitude. Moreover, the rate of expansion of quartz with temperature is seen to be constant in the temperature interval 25°–300°C. This would seem to be in accord with expectation, but it disagrees with Randall's results. While the explanation of these discrepancies does not affect the discussion of the index of refraction of gases, it is still to be desired.

Table 1 summarizes the measurements on the indices of refraction at various temperatures. Measurements were made with pressures

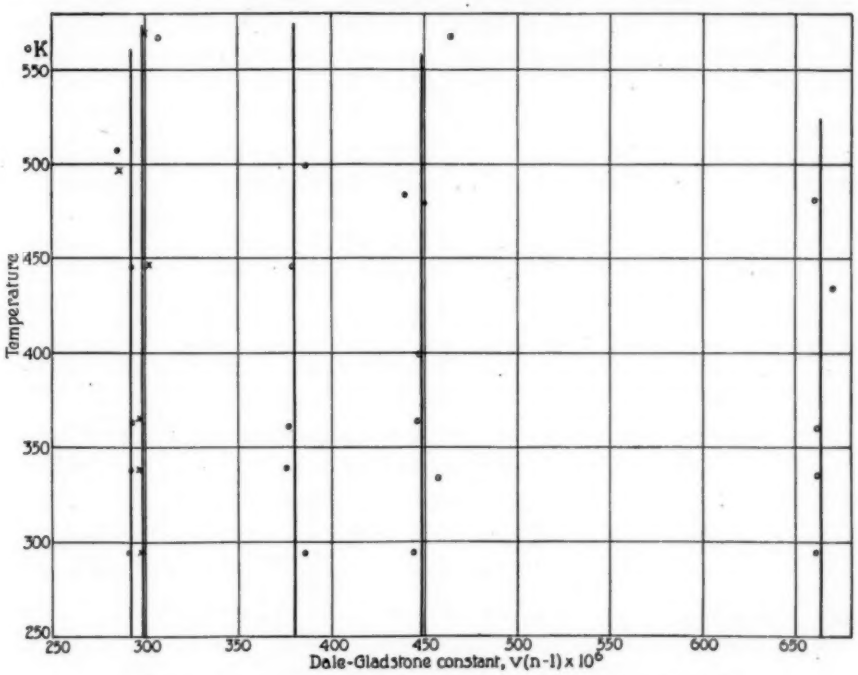

Fig. 4. The constant of the Dale-Gladstone law, $(n-1)v\times10^6$ plotted against temperature for the gases air, N_2, NH_3, CO_2, SO_2.

close to 760 mm and the readings reduced to values at 760 mm by multiplying by the inverse ratios of the pressures. Corrections for compression of the quartz by the gas are not necessary. Column 3 gives the indices of refraction of the wave-length 5852.488A reduced to standard pressure.

The Dale-Gladstone law states that $(n-1)v=$constant where v is the specific volume or is a number proportional to it. Fig. 4 shows $(n-1)v\times10^6$ plotted against temperatures for the various gases.

The volume v for the imperfect gases was computed by van der Waal's equation, taking v at 0°C to be 1 cc. No departure from the linearity required by the Dale-Gladstone formula can be detected from these measurements, or in other words, the thermal coefficient of the index of refraction is the same as the density coefficient. The measurements up to 150°C show less irrationality than do the measurements at higher temperatures. The lines are drawn giving equal weight to the four measurements at the lower temperatures. The intersections of these lines with the line $T=273°K$ give values of the indices of refraction of the various gases at 760 mm for 5852.488A in good agreement with the accepted values for the D line. Similar lines were drawn for the wave-lengths 6143.062A and 6678.276A. Table II gives the values of $(n-1)\times 10^7$ at 0°C, 760 mm for the various gases and various wave-lengths.

TABLE II

Values for $(n-1)\ 10^7$ at 0°C, 760 mm pressure

Gas	λ5852A	λ6143A	λ6678A
Air	2925	2919	2912
N_2	2985	2977	2969
NH_3	3795	3785	3771
CO_2	4485	4473	4465
SO_2	6637	6615	6598

Theory[3] shows that in the infrared there may be a temperature coefficient of the index of refraction differing from the density coefficient for polar molecules, and measurements by Meggers and Peters[4] indicate such a temperature coefficient near the ultra-violet absorption bands in air. It should be interesting to study the temperature coefficient of the index of refraction in these regions.

I wish to express here my thanks to Dr. K. T. Compton for his encouragement and advice.

PRINCETON UNIVERSITY,
September 2, 1926.

[3] P. Debye Phys. Zeit. **13**, 97 (1912).
[4] Meggers and Peters, Bulletin of the Bureau of Standards **14**, 371 (1917).

A DETERMINATION OF THE DIELECTRIC CONSTANT OF AIR BY A DISCHARGE METHOD

By A. P. Carman and K. H. Hubbard

Abstract

Two air condenser systems, one containing the test condenser and the other the balancing condenser, are charged to equal opposite potentials, the opposite charges are mixed and discharged through a galvanometer. The two condenser systems are adjusted until the galvanometer deflection is zero. A special form of rotating commutator was devised for which the contact resistances are small and uniform. This commutator has three pairs of make and break contacts, two for charging and discharging the two condensers, and one pair connected so that a single battery is used to charge both condensers. The capacity of the test condenser is obtained in terms of readings on a condenser which forms part of the balancing condenser system. The ratio of the capacities of the test condenser, with a vacuum and with air for dielectric is then obtained. The calibration for the readings is described. This calibration is made with the apparatus in place, by simple changes of connections. Possible errors from time lag, thermal expansions, and deformations from pressure changes are discussed. The average of thirteen separate measurements gives 1.000594 for the dielectric constant of air at 0°C and 760 mm Hg pressure. The thirteen separate readings agree in the second significant figure of the decimal part of the result.

THE first measurement of the dielectric constant of air was made in 1874 by Boltzmann.[1] He measured the change of potential for constant charge of an air condenser, when the air was exhausted. He obtained the value 1.000590 for the dielectric constant of air at 760 mm pressure and at 0°C. In 1877 Ayrton and Perry[2] determined the dielectric constant of air by comparing, with a quadrant electrometer, the potentials of condensers with and without air. Their value 1.00150 for the dielectric constant of air is generally considered in error. The next determination of the dielectric constant of air was made in 1885 by Klemencic,[3] an assistant working in Boltzmann's laboratory. He obtained the change in capacity of a large air condenser when the air was exhausted, by measuring with a galvanometer the discharges of the condenser. The condenser was charged and discharged sixty-four times per second by a tuning fork commutator. He gives the value 1.000586 as the dielectric constant of air at standard pressure and temperature. Klemencic's individual values vary from 1.000718 to

[1] L. Boltzmann, Wien. Berichte **69**, Part 2, 795 (1874).
[2] Gordon's Electricity and Magnetism, Vol. 1, p. 130.
[3] I. Klemencic, Wien. Berichte Bd **91**; also Rep. d. Physik, Bd. **21** (1885).

1.000478, and he rejects the last ten of his twenty values on account of irregularities. The average of his twenty values is 1.000599.

The next absolute determination of the dielectric constant of air seems to be that of Fritts,[4] who compared the capacities of air condensers by the beats of a heterodyne circuit,[5] recording the beats by an ingenious photographic method. He obtained the value 1.000540 for the dielectric constant of air. In the same year Zahn,[6] also using a heterodyne method, got the value 1.000572.

In view of these variations in values obtained for the dielectric constant of air, and particularly because the methods using high fre-

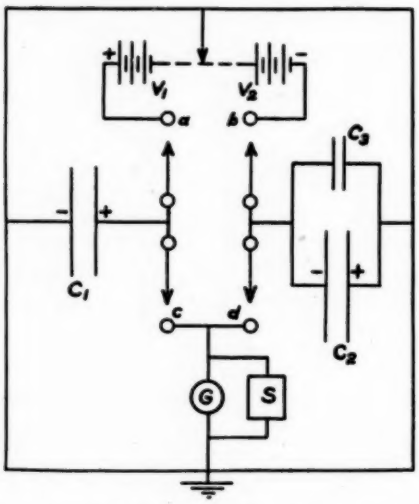

Fig. 1. Diagram of circuit previously used.

quency oscillations have given lower values than Boltzmann's and Klemencic's values, it was thought desirable to make a new determination by one or both of the older methods. This work began in 1923 directly after Fritts' determination in this laboratory. The method used consists in charging two nearly equal air condensers to opposite potentials, and then discharging the two condensers simultaneously through a sensitive galvanometer. The charging and discharging takes place numbers of times per second so that the galvanometer gives a steady deflection for the discharge. The object is to adjust the two opposite discharges until the galvanometer deflection is zero. The

[4] E. C. Fritts, MS Doctor's thesis, Univ. of Ill. Library, Feb. 1923; Physical Review **23**, 345 (1924).

[5] Hyslop and Carman, Phys. Rev. **15**, 243 (1920).

[6] C. T. Zahn, Phys. Rev. **23**, 781; **24**, 401.

arrangement for this method as used by A. P. Carman and K. O. Smith[7] in 1923, is shown in Fig. 1.

At first the well known commutator of Fleming and Clinton[8] was used for the charging and discharging of the condensers, but the galvanometer deflections were so unsteady because of irregular contacts of the brushes of the commutator, that finally an entirely new commutator was devised and used with satisfaction in all this investigation. In the new commutator, contact is made by bringing a platinum-tipped rod end-on against a plate. The rod is connected with insulation bushings to a brass block which fits on an eccentric part of the commutator shaft. The rods are kept horizontal by suitable bearings, and are in pairs, one on the right side and the other on the left side of the eccentric block. The eccentricity in this particular instrument is 3 mm, so that the rods move backwards and forwards through 3 mm in a harmonic motion. The platinum plate is carried through a flat cushioning spring on an adjustable support, so that the end of the rod makes contact with the plate at the rod's maximum outward position. Thus when the contact on the right side is made, the contact on the left side is broken, and vice versa. In the final form of this commutator, as used in this investigation, there are four pairs of rods, so that four connections can be made (or broken) at the same time. It will be seen that in our final circuit, the third pair proved important in allowing the use of a single undivided battery. Various other improvements are found in the final form of this commutator not found in the form described in 1924.[9]

In the equation for the above arrangement of apparatus, it is assumed that the commutator speed and the voltages V_1 and V_2 are absolutely constant for the five or ten minutes of an experiment. Also, the galvanometer was found to vary more or less, unless the shunt was made too low for extreme sensitivity. These difficulties led to the development of a new circuit in which there is a single battery for the charging, and there are better conditions for the balance. The new arrangement has come gradually after many experiments from the first circuit. For the work on this development with the long careful tests and observations involved, credit is due to Mr. Hubbard who took up the investigation with the senior author for the last two years.

The essential parts of the final circuit are shown in Fig. 2. The charging battery of about 50 "B" storage cells is shown at V. The

[7] MS of Master's thesis by K. O. Smith, Library of Univ. of Ill., June, 1923.
[8] Fleming and Clinton, Proc. Phys. Soc. London, **18**, 389 (1903).
[9] A. P. Carman, J.O.S.A., **9**, 175 (1924).

test-condenser C_B is built rigidly and is under a bell jar so that the gaseous dielectric can be exhausted. Its capacity is 0.04 mf. The balancing condenser C_N has approximately the same capacity as C_B. The variable condensers C_D and C_M are in parallel with C_B and C_N respectively and serve for final balancing. The commutator with three pairs of contact rods is indicated by the arrows. The commutator speed was about 1500 r.p.m. The key K_1 is at the start in position Q, so that contacts 6 and 7 are at the same potential. While contacts 5, 6, and 7 are closed, contacts 1, 2 and 3 are open, and vice versa. To insure mixing of the condenser charges, contacts 1 and 2 close just an instant before 3 closes. If the capacity of the test condenser is equal

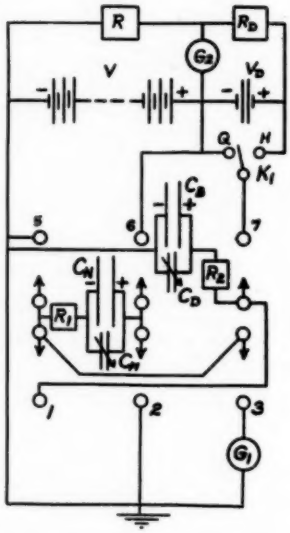

Fig. 2. The new circuit (simplified).

to that of the balancing condenser, there is zero charge remaining after the mixing and consequently no current through the galvanometer. The possible sensitivity can be calculated as follows. Suppose the test and balancing condensers are equal so that there is zero galvanometer current. Now change the capacity of C_B+C_D by C, and the resulting current is I_g. Then $I_g=CVn$, where n is the commutator speed in r.p.s. The galvanometer deflection is $d=I_g/F=CVn/F$ where F is the figure of merit of the galvanometer. The sensitivity of the system to change of capacity is then $d/C=Vn/F$. The figure of merit of the galvanometer is about 10^{-10} amperes per mm deflection. We thus calculate the sensitivity, $d/C=25$ mm galvanometer deflections for

1 mmf change. Let C_1 be the capacity of the test condenser C_B, and K_1 the dielectric constant for a low pressure, and C_2 and K_2 the corresponding capacity and dielectric constant of C_B at normal air pressure. If C_B is the capacity with perfect vacuum as the dielectric then $C_1-C_2=C_B(K_1-K_2)$. Putting this in the above equation for sensitivity, we get $d/(K_1-K_2)=C_BVn/F$. Using approximate values, we get $d/(K_1-K_2)$ equal to 10^6 mm galvanometer deflections per unit change in K. That is, applied to the dielectric constant of air, a change from 1.000590 to 1.000591 should make a difference of one millimeter in the galvanometer deflection. The final results show that we approximate this calculated sensitivity in having variations only in the sixth decimal place.

It is seen directly that the circuit is sensitive to change of voltage. This makes it important to guard against stray induced e.m.f.'s. Thus it was found that for certain commutator speeds, the galvanometer was unsteady. This was traced to voltages induced from the field of the 60 cycle power circuit, these producing considerable galvanometer deflections if the commutator speed was $\frac{60}{2}$, $\frac{60}{3}$, $\frac{60}{4}$, or etc. r.p.s. These stray e.m.f.'s disappeared completely at suitable commutator speeds. The procedure for the calibration of the apparatus and the calculation of the dielectric constant is as follows:

I. With the key at Q, the condenser C_M is adjusted to give zero galvanometer deflection. The pressure of the gas in C_B is P_1 and its dielectric constant is K_1. Then

$$C_BK_1V+C_1K_DV+C_sK_sV=0 \tag{1}$$

where C_B and C_1 are the capacities of the condensers C_B and C_D for vacuum, and C_s is the algebraic sum of all other capacities in the circuit, and K_1, K_D and K_s are dielectric constants of the respective dielectrics.

II. Change pressure of gas in C_B to P_2 with dielectric constant K_2, and bring galvanometer deflection to zero by changing capacity of C_D to C_2. Then

$$C_BK_2V+C_2K_DV+C_sK_sV=0. \tag{2}$$

From Eqs. (1) and (2), we get

$$K_1-K_2=(C_2-C_1)K_D/C_B \tag{3}$$

The calibration to determine $(C_2-C_1)/C_B$ is carried out by adding the resistances R and R_D, the galvanometer G_2, and the two opposing cells giving the resultant e.m.f. V_D.

(1) The key, is on position Q and the condensers are adjusted to zero galvanometer deflection

$$C_BK_BV+C_3K_DV+C_LK_LV+C_{s1}K_{s1}V=0 \tag{4}$$

where C_L is a part of the capacity (C_N+C_M) (see step 3 below), and C_{s1} is the algebraic sum of all remaining capacities in the circuit. K_B, K_D, K_L and K_{s1} are dielectric constants.

(2) The key is turned to position H, and the galvanometer deflection is brought to zero by changing condenser C_D. Then

$$C_BK_BV'+C_4K_DV'+C_LK_LV+C_{s2}K_{s2}V+C_{s3}K_{s3}V'+C_{s4}K_{s4}V_D=0 \quad (5)$$

Here $V'=V+V_D$ and the meanings of the other terms are apparent.

(3) The key is placed at Q, and condenser C_B is disconnected, and capacity C_L of (C_N+C_M) being also removed, the galvanometer deflection is zero. Then

$$C_5K_DV + C_{s1}K_{s1}V = 0. \quad (6)$$

(4) The key is placed at H, and zero galvanometer deflection is produced by changing C_D. Then

$$C_6K_DV' + C_{s2}K_{s2}V + C_{s3}K_{s3}V' + C_{s4}K_{s4}V_D = 0. \quad (7)$$

From Eqs. (4), (5), (6), (7), we get

$$C_BK_B(V' - V) + K_D[V'(C_4 - C_6) - V(C_3 - C_5)] = 0. \quad (8)$$

Substituting $V_D=V'-V$, we get

$$C_B = \frac{K_D[V'(C_4 - C_6) - V(C_3 - C_5)]}{- K_BV_D}. \quad (9)$$

In the above calibration, V and V' are assumed constant, and there were actually no variations of sufficient magnitude to cause appreciable error. If the resistances R and R_D are adjusted to give zero deflection of galvanometer G_2, then R', R and R_D, are proportional to V', V and V_D, where $R'=R+R_D$. Introducing these proportional quantities into Eq. (8), we get

$$C_B = \frac{K_D}{K_B}\,\frac{R'(C_4 - C_6) - R(C_3 - C_5)}{- R_D} = \frac{K_D}{K_B}A\ ; \quad (10)$$

where A is a constant determined by the calibration. Eq. (10) thus gives the capacity C_B in terms of capacity differences as observed on condenser C_D. By combining Eqs. (3) and (10) we get

$$(K_1 - K_2) = (C_2 - C_1)K_B/A. \quad (11)$$

If we use the same gas at the same pressure and temperature we have $K_B=K_1$, then

$$(K_1 - K_2)/K_1 = (C_2 - C_1)/A$$

or

$$K_2/K_1 = (C_1 - C_2 + A)/A. \tag{12}$$

The reduction to standard temperature and pressure is made on the assumption that the dielectric constant is proportional to the density of the gas, and hence directly proportional to the absolute temperature and inversely proportional to the pressure. We get the equation in the form

$$(K_0 - 1) = \frac{760T(C_2 - C_1)}{273(P_1 - P_2)[A - (C_2 - C_1)]} \tag{13}$$

where

$$A = \frac{R'(C_4 - C_6) - R(C_3 - C_5)}{- R_D}$$

as indicated in Eq. (10). We thus get an absolute determination of the dielectric constant of air by the above procedure. The calibration is made with all parts in place, by simply throwing a switch, and is indeed a part of the procedure each time.

In the above method, it is of course assumed that the insulation is "perfect" and this was found by repeated tests to be the case except on some days of very high humidity and consequent surface condensation. No measurements were made on such days. It is assumed that the charging and the discharging are complete in the time of the commutator contact. The inductance and resistance of the circuit were such that no error was caused by time lag. This was verified experimentally.

The importance of the test condenser is such that a brief description of it is desirable. This condenser is constructed of iron plates, each plate being five inches square and one-sixteenth of an inch thick. We will call the two armatures of the condenser, A and B. Armature A consists of fifty plates with forty-nine spaces, each space being three thirty-seconds of an inch wide. The A plates are held together by four quarter-inch steel rods or bolts which pass through holes in the corners of the plates. Iron washers of uniform thickness were carefully turned, and used on the rods between the plates, thus securing uniform spacing. The rods are threaded at the ends, and strong nuts are used to clamp the plates rigidly together. Armature B consists of forty-nine plates held together by rods, with spaces and nuts similar to those for A. The plates of B occupy the spaces between the plates of A, with small but safe air clearance. A common arrangement in an air condenser

of this kind is to have the diagonals of the plates of A at right angles to those of B. To get more effective use of the surfaces, we placed half of the B plates with their diagonals making an angle of 35° to the right of the diagonals of A, and the other half of the B plates making the same angle to the left. These B plates are clamped together on the rods by strong nuts in groups of two or three for rigidity and for uniform spacing. All rods are clamped to a thick plate of Pyrex glass, holes being bored through the glass and the rods are held firmly in place by nuts and washers on each side of the plate. This glass plate is at the top, so that the B plates are in fact suspended from the glass plate. The insulation between A and B was found "perfect" for our purpose. The A armature is joined to earth. The condenser and the glass plate are completely shielded by grounded sheet iron disks and cylinders. The only dielectric in the field, except the air, is the glass between the widely separated rods; and for a condenser of this size the correction for this dielectric is negligible.

The constancy of the capacities of "test" and the "balancing" condenser system is, of course, a fundamental requirement, and this was tested with great care. One annoying variation was finally eliminated by putting the comparison, as well as the test condenser, and the rotating commutator on separated supports, from which it was inferred that the mechanical vibrations introduced a small capacity change in the comparison condenser. The temperature effects on the capacities of the condensers proved troublesome until understood. The condensers are made of several materials, the thermal expansions and contractions, due to even a very moderate temperature change, introduce deformations which persist for a considerable time. The resulting change in capacity is shown by the creeping of the galvanometer deflections. This creep was fairly constant and so could be allowed for, but it was possible to find times and conditions when the creep was very small. A more fundamental difficulty was a capacity change which we ascribed to the displacement of the parts of the condenser by the pressure of the gaseous dielectric. Our test condenser as described above is very strongly built and all parts are of iron except a pyrex glass insulating plate. It was found that, if the gas in the condenser had been at normal pressure for several hours, and it was then evacuated, and allowed to return to normal pressure, there was a galvanometer deflection showing a small capacity change. After the first evacuation and return to normal pressure, the change in capacity was not observed until the condenser had again rested. This effect, though small, is difficult to evaluate. It is an effect equally important in all

methods of obtaining the absolute dielectric constant of a gas, and may exist in small condensers in the same ratio as in large condensers. The important adjusting condenser C_D is of the rotating wing type, and is very carefully built with heavy brass plates turned from cast brass. It has a circular scale and vernier, but the readings for the calibrations were made by means of a telescope and circular scale, a mirror being mounted on top of the rotor shaft of the condenser. The readings were kept in that part of the calibration curve which is a straight line. The bell jar over the test condenser was exhausted by a Hy-vac pump, and the admitted air was carefully dried by passing slowly through tubes containing phosphorus pentoxide. The temperatures were measured by means of sensitive thermocouples, two couples being inside of the bell jar, and one couple on the outside.

This method, as indicated, has been developed slowly after many tests and changes. The special form of commutator devised in the course of the work is satisfactory in making and breaking contact regularly in time and with small and constant resistance. The speed of the commutator can be varied easily through a wide range. Theoretically, changes in speed of the commutator are eliminated in the equation, but these changes in speed are so very small that no appreciable error enters from any secondary effect due to speed change. Speeds of about 1500 were used in the final measurements. The very difficult requirement of constancy in the ratio of potentials of two charging sources has been met by using a single battery for charging both condenser systems, so that variations of the voltage of the charging battery do not come in. The arrangement for calibrating the apparatus in place, by only connecting and disconnecting keys, also reduces possible errors.

Results: After many preliminary trials, the following final measurements were made when the temperature conditions were fairly satisfactory. Early morning hours were used in three of four runs to secure even temperatures. All measurements are included.

	Dielectric constant	Pressure change (mm Hg)
Morning, June 18, 1926	1.000598	732.4
2–6 A.M.	1.000597	730.9
	1.000593	732.9
	1.000595	734.4

Afternoon, June 18	1.000597	738.1
2–4 P.M.	1.000598	737.8
	1.000590	543.2
Morning, June 19	1.000594	731.9
2–4 A.M.	1.000592	730.1
	1.000591	544.3
	1.000592	548.7
Morning, June 27	1.000592	723.2
2–6 A.M.	1.000592	723.5

It will be noted that all of the thirteen separate measurements agree in the second significant figure of the decimal. The final average is 1.000594. Boltzmann's value of 1.000590 is in closer agreement with this value of 1.000594 than the more generally quoted value of 1.000586 of Klemencic. These values by static charge methods are larger than the values by oscillation methods obtained recently by Fritts and by Zahn.

PHYSICS LABORATORY,
UNIVERSITY OF ILLINOIS,
October, 1926.

THE MAGNETIC MOMENT OF THE HYDROGEN ATOM

By T. E. Phipps and J. B. Taylor

Abstract

The magnetic moment of the hydrogen atom has been investigated by the atomic ray method introduced by Stern and Gerlach. Atomic hydrogen formed in a discharge tube by the method of R. W. Wood was first used. The ray was formed in a special all-glass slit system of three slits sealed to the discharge tube. The ray was detected by the reduction resulting on contact with a target coated with molybdenum trioxide. A sharply defined blue line against a white background was the result. In the magnetic field the ray was separated into two branching rays. There was also evidence of a central undeviated ray which is believed to be due to hydrogen active chemically but probably not in the atomic state. From a measurement of the deflection the magnetic moment of the hydrogen atom was calculated to be one Bohr magneton within the limits of experimental error. This result is of interest because of the questions raised by the new quantum mechanics of Heisenberg, Born, and Jordan, and by the spinning electron theory of Uhlenbeck and Goudsmit. Atomic hydrogen formed by the hot filament method of Langmuir was next used. The increased velocity of the atoms in this case resulted in less separation of the ray, but a deflection was distinctly recorded. Finally, the product formed on exposing a mixture of mercury vapor and hydrogen to ultra-violet light was investigated. This is believed by Cario and Franck, Taylor, and others to be atomic hydrogen. Thus far attempts to form a ray which will reduce the target have been unsuccessful. The reasons for this are being investigated.

THE magnetic moment of the hydrogen atom is of great interest since the hydrogen atom is the basis for the calculation of the unit of magnetic moment in Bohr's theory of the atom. Moreover, the magnetic properties of the hydrogen atom have recently become of unusual interest because of the questions raised by the new quantum mechanics of Heisenberg,[1] Born and Jordan,[2] and by the new theory of Uhlenbeck and Goudsmit,[3] which gives the "spinning electron" a magnetic moment of its own. Born,[4] in quoting an unpublished work by Pauli on the theory of the hydrogen atom, has stated that Pauli's theory contemplates a non-magnetic atom. This however does not take into account the theory of Uhlenbeck and Goudsmit, which if accepted will make necessary an addition to Pauli's theory. This state of upheaval in the theories makes direct experiment very desirable.

[1] W. Heisenberg, Zeits. f. Physik, **33**, 879 (1925).
[2] M. Born and P. Jordan, Zeits. f. Physik, **34**, 858 (1925).
M. Born, W. Heisenberg, and P. Jordan, Zeits. f. Physik, **35**, 557 (1926).
[3] Uhlenbeck and Goudsmit, Nature, **117**, 264 (1926).
[4] M. Born, "Problems of Atomic Dynamics," M. I. T., Cambridge, Mass., '26.

In this work the magnetic properties of the hydrogen atom have been investigated. The experimental method was that of atomic ray deflection introduced by Stern and Gerlach[5] in their investigation of the magnetic moments of several of the metal atoms. Stern and Gerlach secured direct evidence of space quantization and orientation when their rays of atoms were divided into separate rays on passage through an inhomogeneous magnetic field. Silver, copper, and gold showed a magnetic separation which yielded a value of magnetic moment closely equal to the Bohr unit magneton. One of the authors[6] verified the work of Stern and Gerlach on silver in a modified apparatus, and in addition found the alkali metals sodium and potassium to possess unit magnetic moments.

The equation relating the amount of deflection of the atomic ray to the magnetic moment of the atom is

$$\frac{1}{M} = \frac{1}{2s}\left(\frac{\partial H}{\partial s}\right)_0 \frac{l^2}{3.5RT}\left\{1+\frac{l^2 M}{12 \times 3.5RT \times s}\left[\left(\frac{\partial H}{\partial s}\right)_l - \left(\frac{\partial H}{\partial s}\right)_0\right]\right\}$$

Here s is the amount of deflection measured as shown later; M is the magnetic moment (gauss-cm per mol); l is the length of the pole pieces of the magnet, the distance the atomic ray must travel through the magnetic field; $(\partial H/\partial s)_0$ is the value of the inhomogeneity of the field at the point where the ray enters the field; $(\partial H/\partial s)_l$ is the corresponding inhomogeneity at the end of the field, after the deflection of the ray. This is not equal to $(\partial H/\partial s)_0$ since $(\partial H/\partial s)$ changes in value from point to point across the field between the pole pieces, being greatest next to the knife-edged pole piece. The values of $(\partial H/\partial s)$ are obtained for any distance of the ray from the knife edge by a preliminary mapping of the field. The 3.5 RT term comes from the expression which Stern[7] found in his direct measure of the velocity of the silver atom. In the present work the hydrogen atom has been found to be magnetic and its magnetic moment has been calculated.

A. Atomic Hydrogen from the Discharge Tube

The discharge tube. Hydrogen was prepared by the electrolysis of barium hydroxide solution, dried when desired by passing through a liquid air trap, and admitted to the discharge tube through a regu-

[5] O. Stern, Zeits. f. Physik, **7**, 249 (1921).
W. Gerlach and O. Stern, Ann. d. Physik, **74**, 673 (1924).
W. Gerlach, Ann. d. Physik, **76**, 163 (1925).
[6] J. B. Taylor, Phys. Rev., **28**, 576 (1926).
[7] O. Stern, Zeits. f. Physik, **2**, 49 (1920).

lated leak. In most of the work with the discharge tube, the hydrogen was not dried, in accordance with the procedure of R. W. Wood.[8] The discharge tube was similar to that used by Wood, Bonhoeffer[9] and Copaux.[10] It was made of 18 mm Pyrex tubing and had a total length of 3.5 meters. The electrodes were cylinders made from aluminum sheet and crimped to tungsten lead-out wires. The electrode tubes were bent over as shown in Fig. 1, to prevent small particles dislodged from the electrode surface from falling into the central portion of the discharge tube. Such metallic particles were undesirable since they catalyze the recombination of atomic to molecular hydrogen, as was shown by the change in color of the discharge in the vicinity of such

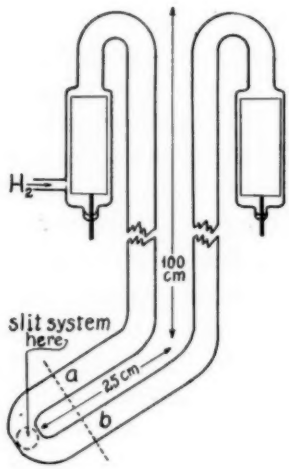

Fig. 1.

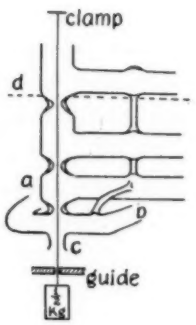

Fig. 2.

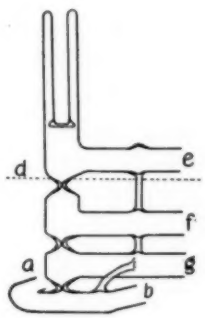

Fig. 3

Fig. 1. The discharge tube.
Fig. 2. Method of preparing the glass slit system.
Fig. 3. Completed slit system, showing preliminary target.

particles from deep pink to white. These particles were seen to glow intensely in the discharge on account of the heat liberated on their surface. The tube was operated on a 1 kw transformer at 25000 volts. The pressure of undried hydrogen was 0.12 mm. Under these conditions a pure spectrum consisting of intense lines of the Balmer series against a black background was observed by means of a Zeiss pocket spectroscope. When the tube was first put into operation the complex secondary spectrum sometimes appeared in the background, but with

[8] R. W. Wood, Phil. Mag. **42**, 729 (1921).
[9] K. F. Bonhoeffer, Zeits. f. Phys. Chem. **113**, 199 (1924).
[10] Copaux, Perperot, and Hocart, Bull. soc. chim. **37**, 141 (1925).

prolonged operation of the tube this disappeared and pure Balmer series remained. This phenomenon was first described by R. W. Wood.

The slit system. To form the atoms present into a ray, an all-glass slit system was sealed to the central portion or foot of the discharge tube as indicated in Figs. 1, 2, and 3. When a metal slit system was sealed to the midpoint of the discharge tube, the discharge for an inch or more to each side was distinctly white. For this reason glass as a material for the slit system was preferred to metal.

Each of the three slits used was 0.075 mm wide and 3 mm long. They were constructed by placing a steel ribbon of these dimensions through a glass apparatus (Fig. 2), which had been constricted at three points. This ribbon was suspended from one end as shown, stretched taut by a weight on the other end, and adjusted to hang perfectly straight through a guide which permitted no twist. Then beginning at the top each constriction was heated in turn and the glass pinched with knife-edged tweezers on to the ribbon. Each pinch was followed by careful heating and annealing to relieve all strain in the system. This procedure gave the three slits the perfect alignment necessary for the formation of a sharply defined ray of atoms. Finally, after the three pinches had been made, the whole tube carrying the slits was given a prolonged annealing in a large air-free gas flame. When cooled to approximately 100°C it was then immersed in a hot bath of hydrochloric acid to dissolve out the steel ribbon. The glass rod supports shown between the side tubes (Figs. 2 and 3) served to keep the slit system rigid during and after the pinching treatment and yielded support to the fragile slits. These supports were not heated during the annealing. The system was sealed off at *c* (Fig. 2) and later made part of the discharge tube as shown in Fig. 1, by sealing on at *a* and *b*.

From each slit-chamber tubes led off through liquid air traps to separate high-speed mercury vapor pumps. This use of separate pumps maintained a progressively increasing vacuum in the system. In the discharge tube itself a pressure of 0.12 mm was produced through the leak valve from the hydrogen generator. The pump between the first and second slits then reduced this pressure to approximately 0.005 mm in the first chamber. On account of this reduced pressure, atoms leaving the discharge tube through the first slit and directed towards the second slit suffered only slight interference in their path. Then between the second and third slits another pump caused a reduction to less than 0.0001 mm. The increased free path in this chamber further favored the progress of the directed ray of atoms, and the third slit served to define the ray still more sharply. Stray hydrogen atoms may

have been removed also by recombination on the glass walls. This would aid in the production of a well-defined ray.

The target. This unidirectional ray entered the chamber above the third slit where it was received on a target of molybdenum trioxide (Fig. 3). The target was a ground fire-polished surface of glass which was coated with a very fine-grained deposit of molybdenum trioxide. The deposit was formed by holding the cold target intermittently in the smoke produced by igniting a piece of molybdenum sheet in a hot oxygen-gas flame. Very fine smoke particles resulted from the ignition. A surface when prepared properly showed no grain under a magnification of 26× and was almost pure white, with a very slight yellow tinge. The image which the ray of atomic hydrogen formed on the target by reduction of the trioxide to a lower oxide, was a dark blue and was distinctly visible against the white background.

Assembly of the apparatus. In the preliminary tests without the magnetic field, the target was introduced as a re-entrant tube (Fig. 3, above the dotted line). The distance from the third slit to the target was 3 cm to reproduce the length of path required later in the magnetic measurement. With this preliminary apparatus the conditions for forming an image of the atomic ray were studied. When satisfactory conditions had been determined the upper portion was removed at *d* (Fig. 3) and the remaining slit system was cemented into the brass box (Fig. 4) containing the pole pieces.

This pole piece box had been used previously by one of the authors[6] in the determination of the magnetic moments of the alkali metals, and it was modified only slightly to allow the replacement of the pair of metallic slits used in that investigation by the new glass slit system.

The slit system was held rigidly in a brass collar and plate with high melting de Khotinsky cement. Adjustment of the slit path to parallelism with the knife edge and to the desired distance from the knife edge was accomplished by motion of this plate, which was slotted about four screws set into the body of the box. When the slit path had been properly adjusted, the screws were tightened and all joints were made vacuum tight with a beeswax-rosin mixture. The pole-piece box with its slit attachment was then clamped between the broad faces of the electromagnet,[11] and sealed to the discharge tube at *a* and *b* (Fig. 1), and to the vacuum pumps at *e*, *f*, and *g* (Fig. 5). The target consisted of a re-entrant glass tube of the form shown in Fig. 4. The preparation of the molybdenum trioxide surface has been described above. The

[11] The same electromagnet used in the previous investigation already mentioned.

target was sealed into the annular channel at the top of the pole-piece box with beeswax-rosin mixture.

Fig. 5 shows the complete connections for a magnetic measurement with atomic hydrogen from the discharge tube. Pump No. 1 evacuated directly the first slit-chamber, and through stopcock S served to evacuate the discharge tube and connections to the hydrogen generator. Pump No. 2 evacuated the second slit-chamber and the pole-piece box. High range McLeod gauges were used to determine the vacuum conditions in the slit-chambers and pole-piece box.

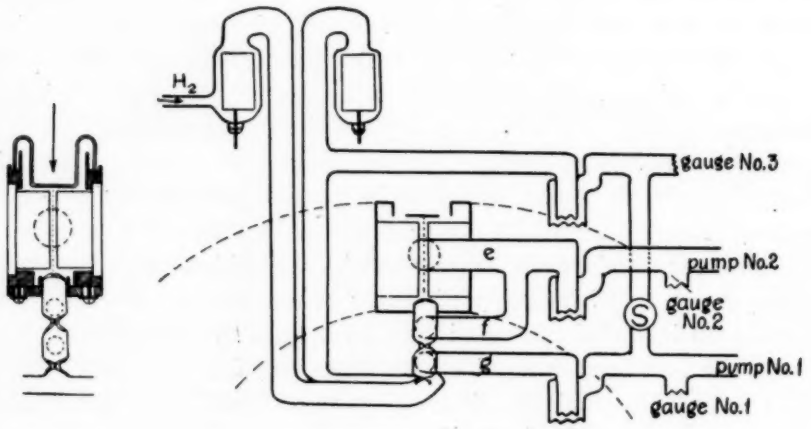

Fig. 4. Fig. 5.

Fig. 4. Pole-piece box with slits and target attached.
Fig. 5. Diagrammatic sketch of complete connections. Dotted lines indicate position of electromagnet.

Procedure. With S open, a high vacuum of the order 10^{-6} mm or less was obtained in the entire system. S was then closed and the hydrogen leak regulated until an approximate pressure of 0.12 mm was obtained in the discharge tube, as recorded by McLeod Gauge No. 3. The discharge could not be maintained at pressures very much lower than this; while at higher pressures the ray became more diffuse, as was shown by a greater general reduction over the face of the target. For a run without magnetic field the discharge was then started. For a run with magnetic field the field was applied before the discharge was started. In the latter case, on account of the large heating effect caused by the magnetic field, it was found necessary to cool the foot of the discharge tube with running water. At the end of about twenty minutes a light line image caused by the ray could be seen distinctly by looking down on the target (as shown by the arrow in Fig. 4). It was

rather surprising that the image could be seen from the reverse side in this manner. This very desirable result was due doubtless to the extreme thinness of the molybdenum trioxide deposit and to the penetrating power of the ray of atomic hydrogen. At the end of approximately four hours the image appeared to have reached its maximum density. The target was then removed, the image was examined under the microscope, and measured with a micrometer eyepiece. Photomicrographs were then made of the image and of a comparison scale (0.1 mm divisions), by which means the micrometer measurements were confirmed.

Discussion of images. Fig. 6, I and II are photomicrographs 7× of images secured without and with the magnetic field respectively. These photomicrographs were taken with light transmitted through the glass target and oxide coating. Separation into two lines is very distinct. A remarkable difference in the appearance of the image was noticed depending on whether it was viewed by transmitted or reflected light.

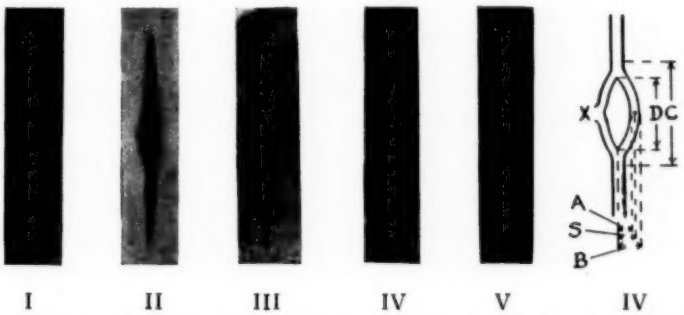

Fig. 6. I, II, III. Photomicrographs (7×) of images secured with hydrogen discharge tube. I. Without field. II. With field, showing separation of ray. III. With field showing separation overshadowed by diffuse central ray.

IV, V. Images secured with atomic hydrogen from a hot filament. IV. Without field. V. With field, showing broadening secured with high velocity atoms.

VI. Diagrammatic sketch of II. $s=0.19$ mm, $c=2.2$ mm, $D=0.9$ mm, $A=0.08$ mm, $B=0.30$ mm.

Fig. 6, II shows clearly the two lines which were always most prominent by transmitted light. Fig. 6, III shows the entirely different appearance by reflected light. Here a central undeviated line with diffuse edges overshadows the deviated branches to such an extent that a casual observer might fail to notice them.

The following tentative explanation of this phenomenon is offered. The two branches seen in Fig. 6, II (transmitted light) are due to atomic hydrogen. The undeviated central line of III (reflected light) is due to hydrogen active chemically toward molybdenum trioxide, but probably not in the atomic state. The dissociation of molecules into atoms in the discharge is far from complete. Bonhoeffer[9] estimates that 20 percent

only is dissociated under conditions similar to those of this experiment. The ray then consists in large part of hydrogen molecules. It is conceivable that high speed hydrogen molecules or excited molecules produced in the discharge might be active chemically but show no appreciable deviation in the magnetic field, thus accounting for the central undeviated line.

If this explanation is received as plausible, it remains to explain why the two branches (Fig. 6, II) ascribed to atomic hydrogen should be indistinct by reflected but very plain by transmitted light; whereas the undeviated line (Fig. 6, III) ascribed to molecular hydrogen should be far more distinct by reflected than by transmitted light. If it be assumed that atomic hydrogen penetrates the molybdenum trioxide coating to a greater depth than does molecular hydrogen, it is apparent that there will be much greater depth to an image formed by atomic hydrogen than to one formed by molecular hydrogen, and this depth of image will best appear when it is viewed by transmitted light, under which condition one observes the accumulated effect of reduction in all the layers. On the other hand, reduction due to molecules would be more superficial in character, and such an image would appear strong by reflected light, but would show very little opacity by transmitted light.

To test the idea that the central line might have been caused by high velocity hydrogen molecules, the hydrogen entering the lowest slit was heated to 400°C in the absence of a discharge. (The temperature of the discharge had previously been shown to be about 400°C. See below.) After 17 hours no image was visible on the target. This result shows that normal hydrogen molecules at the temperature of the discharge probably could not have caused the central line. It seems not unlikely that this undeviated line may have been due to excited hydrogen molecules from the discharge. The peculiar character of the central line as described above, and our present conception of the hydrogen atom seem to preclude the possibility that it was caused by atomic hydrogen.

The flattened cusp at the center of the left branch (Fig. 6, II) marked "X" in Fig. 6, VI, shows the position of the knife-edged pole piece. At this point the ray has actually been drawn against the knife edge by the greater inhomogeneity of the field at the edge. For this reason the more uniformly deflected right hand branch was chosen for the measurement of s. Fig. 6, VI is a diagram of II with dimensions. The distance s is the quantity used in the calculation of M, the magnetic moment.

Temperature of the discharge. Before a calculation of magnetic moment could be made, it was necessary to measure the temperature in the discharge tube. This temperature appears to be very uncertain on account of the violent electrical conditions existing in the discharge. To get an approximation of the temperature a glass-sheathed thermocouple (chromel-alumel, B. & S. No. 28) was sealed into the discharge tube and made to extend centrally down the entire length of the foot of the discharge tube (Fig. 1), a length of about 25 cm. The junction was not more than 3 cm distant from the point at which the slit system was sealed. A glass sheath was used in order to avoid to a large degree the false temperature effect which would have been observed with a

bare thermocouple on account of recombination of atomic hydrogen on its surface. The temperature recorded was about 390°C at the pressure (0.12 mm) used in the magnetic experiments.

Calculation of the magnetic moment. The data for the calculation of M, the magnetic moment of the hydrogen atom, are as follows. l, the pole piece length, 3 cm; the distance from the middle of the slits (i.e. of the ray) to the knife edge, 0.29 mm, corresponding to the value $(\partial H/\partial s)_0 = 140{,}600$ gauss/cm; $s = 0.19$ mm; $(\partial H/\partial s)_l = 107{,}800$ gauss/cm; T the absolute temperature, 663°K. Upon substitution of these values into the equation given above, there results $M = 6050$ gauss-cm. This is 8 percent higher than 5600 gauss-cm, the magneton value calculated on the basis of Bohr's theory.

Errors. Should a high precision determination of the moment of the hydrogen atom be made, the following errors must be eliminated. (a) Errors in $(\partial H/\partial s)_0$ and $(\partial H/\partial s)_l$ may amount to 2 percent. (b) Three independent measurements of s by different observers from the same photomicrograph agreed within 2 percent. s cannot be measured with extreme accuracy at present since the deflected ray is slightly diffuse at its edges and is broader than the original ray. This "spreading" is a consequence of the Maxwellian distribution of velocities, i.e. the s for individual atoms is spread over a range of values. This can be remedied by producing a ray of single (or narrow-range) velocity atoms. Narrower slits would also reduce the uncertainty in the measurement of s by decreasing the width of the image of the deflected ray relative to the total splitting. The detection of the ray on targets of molybdenum trioxide was very satisfactory. The images formed were easily visible and permanent. (c) The temperature (velocity) error. There is an uncertainty of perhaps as much as 25° (approximately 4 percent) in the above value of the temperature of the discharge from the following causes. Slight fluctuations in pressure were unavoidable; and it was found that the temperature varied inversely as the pressure. Another uncertainty was the unknown extent to which the glass sheathing of the thermocouple catalyzed the recombination of the hydrogen atoms. This operated no doubt to make the observed temperature higher than the true temperature of the discharge. Since this factor was though to be a very important one, 390°C probably represents a maximum value for the temperature of the discharge. Losses by conduction away from the thermocouple junction were minimized by leading the thermocouple wires through a considerable length of the discharge tube. For obvious reasons a metal radiation shield could not be introduced into the discharge, and consequently radiation losses

were uncertain and perhaps large. On account of the uncertainty of measuring the temperature of the discharge, a direct determination of the velocity of the atoms leaving the discharge tube (by a method similar to that used by Stern[7] with silver atoms) will probably be the best way in the future of eliminating the temperature error.

The summation of errors in the above determination of the magnetic moment of the hydrogen atom may amount to 10 percent. Within experimental error then the hydrogen atom has been shown to have a magnetic moment equal to one Bohr magneton. This experimental result appears to be in harmony with Bohr's conclusions as to the magnetic properties of the hydrogen atom, and provides a condition that must be met by the newer quantum theories.

B. Atomic Hydrogen from a Hot Filament

Following the tests on atomic hydrogen made in a discharge tube, atomic hydrogen formed by the hot filament method of Langmuir[12] was investigated. The discharge tube was replaced by a simple glass chamber containing a tungsten filament spot-welded through nickel intermediate supports to tungsten lead-in wires (B. & S. No. 18). The filament consisted of 15 turns of 7 mil wire closely wound on a core of approximately 1 mm diameter. The filament was heated by a current of 2.5 amperes to a temperature estimated at 2800°C. It was placed within less than 1 mm of the first slit. Hydrogen was admitted as described for the discharge tube and the same pressure was used. To prevent possible poisoning and deterioration of the filament the hydrogen was first dried by passing it through a liquid air trap. The chamber was water-jacketed.

With all other conditions identical with those of Section A, an image on the molybdenum trioxide target was visible in about 40 minutes. However, as indicated in Plate 5, a splitting of the image did not appear. Because of the greatly increased velocity of the atoms formed on the glowing filament, the deflection of the ray in the magnetic field appeared only as a slight broadening. On account of the presence in the ray of extremely high velocity molecules, probably capable of reducing molybdenum trioxide, a heavy undeviated central line helps to overshadow the separation. Plate 4 shows the image in the absence of a magnetic field. With narrower slits the broadening might be resolved into a separation which would allow a calculation of the magnetic moment.

[12] I. Langmuir, J. Am. Chem. Soc., **38,** 2221 (1916).

C. Active Hydrogen by the Mercury Vapor, Hydrogen, Ultra-violet Light Method

Recently Cario and Franck,[13] Taylor and Marshall,[14] Bonhoeffer,[15] and others have investigated the chemical reactions of the product formed on exposing a mixture of hydrogen and mercury vapor to ultra-violet light. The nature of the reactions obtained indicated the presence of atomic hydrogen. To conclude the present investigation, it was thought desirable to test the magnetic properties of active hydrogen produced by this method. The chamber containing the tungsten filament was replaced by a shorter chamber with a quartz end-plate and a reservoir of mercury. This chamber was heated to 45°C (the temperature employed in Cario and Franck's experiment), and exposed to the ultra-violet light from a water-cooled mercury arc. The quartz window of the arc was placed in contact with the quartz end-plate of the slit system. A pressure of hydrogen from 0.1 to 0.2 mm was maintained. The slit system and the rest of the apparatus were the same as in Sections A and B.

Preliminary trials in which re-entrant rods coated with molybdenum trioxide were sealed into the lower chamber resulted in almost instantaneous reduction of the white trioxide to the blue lower oxide. The test rods were then removed. After several runs with a slit system and target, one of which lasted for 43 hours, no trace of an image was secured on the target. This unexpected result led to a short investigation of the reasons for the failure to obtain a ray of the active product. A bare thermocouple (platinum, platinum-rhodium, B. & S. No. 36) was sealed into the reaction chamber in order to note any rise of temperature due to recombination of hydrogen atoms on its surface. No rise was noted. The same thermocouple sealed into a side tube leading from the discharge tube (Section A) and at 10 cm distance from the discharge showed a rise of temperature of more than 600°C. Furthermore a small amount of molybdenum trioxide introduced into the ultra-violet reaction chamber showed only slightly more than a surface reduction after an eight hour period of exposure. Boats of the trioxide similarly placed in side arms of the discharge tube showed reduction to a depth of a millimeter in a few minutes time.

The conclusion which may be drawn from the behavior of thermocouples, and from the chemical activity in the discharge tube and

[13] Cario and Franck, Zeits. f. Physik **11**, 161 (1922).

[14] H. S. Taylor and A. L. Marshall, J. Phys. Chem. **29**, 1140 (1925); J. Phys. Chem. **30**, 34 (1926).

[15] K. F. Bonhoeffer, Zeits. f. Phys. Chem. **119**, 474 (1926).

the ultra-violet chamber respectively, is that atomic hydrogen if present in the latter case can be there in small amounts only. This may explain the failure to secure a detectable ray of atomic hydrogen in a reasonable length of time from the ultra-violet chamber. However, since our preliminary experiments with oxide coated rods showed that appreciable amounts of molybdenum trioxide were reduced by *some* active substance in the ultra-violet chamber, the failure to produce a beam may also be explained by the assumption that the active substance consisted not of atomic hydrogen but of short-lived excited hydrogen molecules[16] or of mercury hydride.[17] Either of these products might be expected to possess sufficient chemical activity to reduce molybdenum trioxide when first formed in the lower chamber, but might have too short a life to form a ray. This question is receiving further investigation.

In conclusion the writers wish to thank the Department of Physics for the use of the large Dubois magnet. They also wish to acknowledge the grant of funds from the Graduate School of the University of Illinois, which has made this research possible.

LABORATORY OF PHYSICAL CHEMISTRY,
UNIVERSITY OF ILLINOIS,
November 15, 1926.

[16] E. K. Rideal and Hirst, Nature, **117**, 449 (1926).
[17] K. T. Compton, Phil. Mag., **48**, 360 (1924).
K. F. Bonhoeffer, Zeits. f. Phys. Chem., **116**, 391 (1925).

THE MAGNETIC PROPERTIES OF EVAPORATED NICKEL AND IRON FILMS

R. L. EDWARDS

ABSTRACT

Coercive force, retentivity, and hysteresis loop forms for evaporated films of Ni and Fe.—Films of nickel and iron, produced by evaporation at low pressure, were studied with the object of verifying the reported existence of an abrupt change of coercive force at a critical thickness, and also to discover the cause of certain peculiar hysteresis loop forms. *Critical thickness* was found for iron films at approximately 50 mμ, in satisfactory agreement with Sorensen. At this thickness the coercive force changes abruptly from the high value of approximately 100 for thinner films. The observations were made upon films deposited on a base of aluminum foil, .0025 cm in thickness. The foil was heated previous to and during deposit. No such critical thickness was observed in nickel. Peculiar *hysteresis loops* were found. Nickel films unheated have very narrow loops, with magnetic induction nearly proportional to the field up to 139 gauss, where the induction is one-third to one-half that of the metal in bulk. Films heated previous to and during deposit give a magnetic induction at 139 gauss that is approximately three times as great, or like that of metal in bulk. But the retentivity and coercive force increase five-fold and become less like those of the metal in bulk. In similarly heated films of iron, these last two magnetic properties are also much greater than with metal in bulk. The peculiarities of the films are probably caused by the nature of the crystalline state. To what extent the phenomena depend upon the presence of the aluminum base is yet to be ascertained. The present view is that the presence of gas alters the crystal growth. On the whole the experiments seem to emphasize the importance of the influence of the crystalline state upon magnetic properties.

THE investigation of thin films of the ferromagnetic elements has disclosed two peculiar properties,—a very large change in magnetic induction at a fairly well defined critical thickness, and under certain conditions broad, nearly rectangular, hysteresis loops. The earlier work[1] done in this field was on films electrolytically deposited, and the above effects were attributed[2] to the influence of various occluded gases present, especially hydrogen. If, however, these properties are inherent in the metals themselves, the establishment of this fact is of importance in the theory of magnetism.

In order to test the magnetic as well as other properties of the ferromagnetic elements, deposited in the absence of contaminating influences,

[1] Seckelson, Ann. d. Physik **67**, 37 (1899). Maurain, Jour. d. Physique, **10**, 123 (1901); **1**, 90 (1902). Schild, Ann. d. Physik, **25**, 586 (1908); **1**, 151 (1902). Gans, Phys. Zeits. **12**, 911 (1911); and others.

[2] Kaufman and Meier, Phys. Zeits. **12**, 513 (1911).

this laboratory has been making a study of films produced by evaporation. Sorensen[3] found some evidence of a thickness critical for coercive force in evaporated films of nickel at about 200 mμ and in iron at 55mμ. The coercive force changed abruptly to lower values as the thickness was increased.

The first purpose of the present investigation was to check these critical thicknesses. If they exist, are they independent of the various conditions accompanying deposition, such as the heat-treatment of the film, the emission velocity from the evaporating filament, and the residual gas pressure?

The apparatus used in this study was not essentially different from that used by Sorensen, to whose paper the reader is referred for details. The evaporation occurred in a horizontal cylindrical glass vessel, containing two film carriers, one below the hot filament and one above. An electric heater was placed under the lower one. The carriers moved back and forth perpendicularly to the filament and in a manner insuring a uniform deposit. Later observations by Mr. K. J. Miller have shown that the variation in film thickness does not exceed 5 percent except at the extreme edge of the film. As a base for the films, aluminum foil one mil in thickness was employed. The lower film is the hotter as the upper one is not only further from the heater, but it is also shielded from it by the lower foil. Temperatures of the lower foil were measured for various heating currents by means of a thermocouple. Temperatures at the upper position though not determined were in all cases much lower.

To reduce the initial magnetization observed by Sorensen in some of his films, brass parts were substituted for iron in the evaporation apparatus, but as noted later, this substitution failed to accomplish its purpose.

Results for Nickel

In order to determine the critical thickness of nickel, if such existed, a large number of films were deposited and tested. It was found that the thickness affected the magnetic properties only slightly if at all, but variations of the heat-treatment during deposition had very considerable effects. The films are therefore classified according to their heat-treatments.

The results are presented in Table I. Subsequent to nickel film No. 6 all films deposited in the lower position are listed under an odd number, those deposited above, under an even. The only films discarded were those which had oxidized, or those deposited during improper function-

[3] Sorensen, Phys. Rev. **24**, 658 (1924).

ing of the evaporation apparatus. The graphs are plotted with ordinates 4π times the intensity of magnetization, rather than induction.

TABLE I

Nickel films having minimum heat treatment. δ is the film thickness in mμ; β_{139}, the magnetic induction at 139 gauss; I_r, retentivity in percent; H_c, coercive force in gauss

Film No.	δ	β_{139}	I_r	H_c	Film No.	δ	β_{139}	I_r	H_c
8	23	1350	16	5	36	104	1940	26	24
2	39	1240	18	5	44	123	2100	32	32
5*	40	1330	30	11	13**	132	1680	31	35
40	67	2120	25	32	38	139	2100	28	29
14	75	1140	12	17	34	147	1520	12	10
32	77	2040	36	26	10	222	1300	25	28
20	90	1250	14	12	*Bulk nickel*				
22	96	1310	31	35	Annealed		4900	31	1.2
28	99	1430	32	35	Unannealed		3600	68	30

* 5 is an upper film.
**Heater not in action during deposition of 13.

Though most of the "unheated" films of Table I were subjected to the indirect heating effect of the heater in addition to that of the filament, the similarity of their loop forms would indicate that their temperatures did not differ widely. Films No. 34 and No. 10, Fig. 1, *a* and *b*, show the limits between which most of them lie. In Fig. 1, *c* is a hysteresis loop of a well-annealed specimen of the nickel wire (dimensional ratio 265) used for filaments, while *d* is a loop of an unannealed specimen of the same wire. All graphs of Fig. 1 are plotted on the same scale of magnetization and field strength.

The increasing retentivities and coercive forces with increasing thickness observed in Table I are probably due to the more prolonged heating which the thicker films necessarily received, since No. 34, $\delta = 147$, for which the tube was water-cooled throughout, though a comparatively thick film, has the narrow form of loop shown by the thinner films. In those least heated, the coercive force and the area of the hysteresis loops are almost vanishingly small. In this respect they resemble well-annealed nickel. The dissimilar forms of their loops however make this similarity meaningless. The annealed bulk nickel is nearly saturated at a low field, while in the films, the magnetic induction is nearly proportional to the field up to the strongest fields that were available, yet at all points low compared with that of bulk metal.

All foils were heated in contact with a carbon lamp some twenty minutes before the pre-deposit weighing. Yet later work indicated that the occluded gas and water vapor still remaining on the foil largely affected

the magnetic properties of the film deposited thereon. To test this evidence, two films were deposited unheated on foils which had been heated

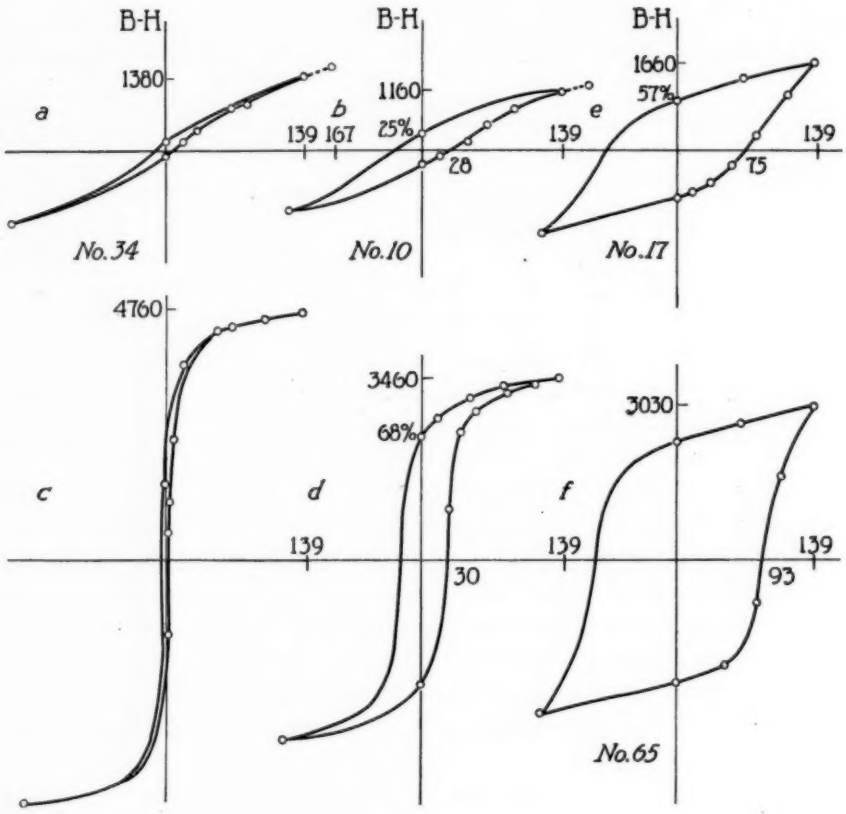

FIG. 1. Hysteresis curves for nickel films.

to 325° for forty minutes in the evaporation apparatus before depositing the films. The following results were obtained:

Film No.	δ	β_{139}	I_r	H_c
72	83	2130	44	46.5
71	161	2680	58	49

Changing the position of No. 72 in the evaporation apparatus during the interval between the heating and the evaporation process permitted its exposure to the atmosphere for several minutes and probably accounts for its lower induction, retentivity, and coercive force. Nevertheless both films show a decided increase in these properties over the films also deposited unheated but whose foils did not receive such a pre-deposit heat-

treatment. Their characteristics are very similar to those of the heated films of Table II following.

In order to determine the loss in weight of the foil due to extreme heating, two foils were heated to 325° for an hour in the evaporation apparatus and then reweighed. The loss in weight in neither case exceeded 0.05 mg, which corresponds to the weight of a nickel film of about 3mμ in thickness.

TABLE II

Nickel films heated during deposition, foils not previously baked. δ is the film thickness in mμ; β_{139} and β_{167}, the magnetic induction at 139 and 167 gauss, respectively; I_r, retentivity in percent; H_c, coercive force in gauss

Film No.	δ	β_{139}	β_{167}	I_r	H_c	Film No.	δ	β_{139}	β_{167}	I_r	H_c
6	51	1700	1950	67	67	17	135	1800	2300	57	75
4	63	2300	2460	59	55	35	176	2550	2700	54	79
1	68	1740	1900	48	58	27	180	2430	2820	67	78
31	99	2510	3100	55	58	9	388	2160	2500	67	67
11	103	2010	2230	40	75						

Table II lists those films which were heated during deposition to a temperature of about 200°, but the foils of which were given no pre-deposit heating. Fig. 1 *e* shows the graph for a representative film of this group, No. 17, ($\delta = 135$). There is no evidence of any critical thickness shown in this table.

Table III presents the data for the films whose foils were heated for corty minutes at 200° previous to deposition, as well as heated to the same temperature during deposition. These show a further large increase in foercive force and retentivity. Fig. 1 *f* is for film No. 65 ,($\delta = 257$), which

TABLE III

Films heated during deposition, foil previously well baked. δ is the film thickness in mμ; β_{139} and β_{167}, the magnetic induction at 139 and 167 gauss, respectively; I_r, retentivity in percent; H_c, coercive force in gauss

Film No.	δ	β_{139}	β_{167}	I_r	H_c	Film No.	δ	β_{139}	β_{167}	I_r	H_c
51	50	1830	2800	59	81	73	179	2200	2650	80	96
63	63	1220	1900	72	104	53	182	2620	3100	75	87
47	76	2300	3600	81	99	69	183	2700	3200	76	96
67	78	1500	2100	58	87	87	219	2480	2850	70	88
41	94	2120	2800	72	104	59	224	2960	3350	73	84
45	97	2100	2680	62	94	43	230	2600	2780	67	81
39	104	2350	2850	65	104	37	244	3100	3500	78	93
61	107	1560	2200	69	104	65	257	3170	3520	78	93
21	123	2100	2600	71	104	77	259	2480	2950	68	89
15	161	2600	3000	76	83	55	276	2650	3000	74	78
81	168	2460	2820	71	90	89	304	2960	3300	75	89

may be taken as representative. These films were very hard both mechanically and magnetically. They were initially strongly magnetized, and the unsymmetrical hysteresis loops obtained for many would indicate

that demagnetization was imperfectly accomplished. No critical thickness is indicated.

Oxidation invariably accompanies deposition at temperatures of 300° with the tube exhausted no better than was feasible in this work. The magnetic effects are greatly reduced retentivity and coercive force,—the former by a fourth or fifth, the latter by a half. There is no decrease in the calculated magnetic induction, though a part of the weight of the film from which the magnetic induction is calculated is nickel oxide. The induction is low however compared with that of bulk metal.

The brass surfaces in the evaporation apparatus adsorbed much gas and prevented the attaining of vacua much better than .001 mm and when the tube was heated during the deposition of a film, rapidly rising pressures invariably occurred. When pressures reached about .005 mm, the evaporation and heating processes were interrupted to permit reduction of the pressure. The most serious result was in the unequal heat-treatments which different films, supposedly treated alike, received, and it is to these variations rather than to the pressure variations that the comparatively wide range of results for heated nickel films is probably due. Later test cases showed the magnetic characteristics to be practically independent of pressure up to at least .015 mm, that is, the magnetic properties of such films were certainly no less uniform.

After some of the nickel films used in this investigation had stood in air for six weeks, they showed a magnetic induction lowered by about ten percent. There was however no change in the retentivity or coercive force. The slow change in properties of nickel films was also observed by Peacock[4] in his work on the Hall effect, and by Manning in his yet unpublished work on optical effects.

Results for Iron

The brass parts introduced in the evaporation apparatus to reduce the initial magnetization, not only failed to accomplish their purpose with the nickel films, but also owing to adsorbed gases introduced serious difficulties in the pressure control. The brass parts were accordingly replaced with iron for the work on iron films. Pressures through this portion of the investigation were maintained at less than .001 mm.

Preliminary tests indicated a broadening of the hysteresis loops with increasing heat-treatment as was the case with nickel. But in order to test for the presence of a critical thickness, most of the iron films were given the same type of heat-treatment,—heating the foil to 200° for an hour and then depositing the film at the same temperature. As in the case

[4] Peacock, Phys. Rev. 27, 474 (1926).

of nickel, the iron films of Table IV are listed in order of their thickness as calculated from their weighings. There is striking evidence of a critical thickness shown by this table. Typical hysteresis loops (No. 5 and No. 9) below and above the critical thickness are shown in Fig. 2, *a* and *b*.

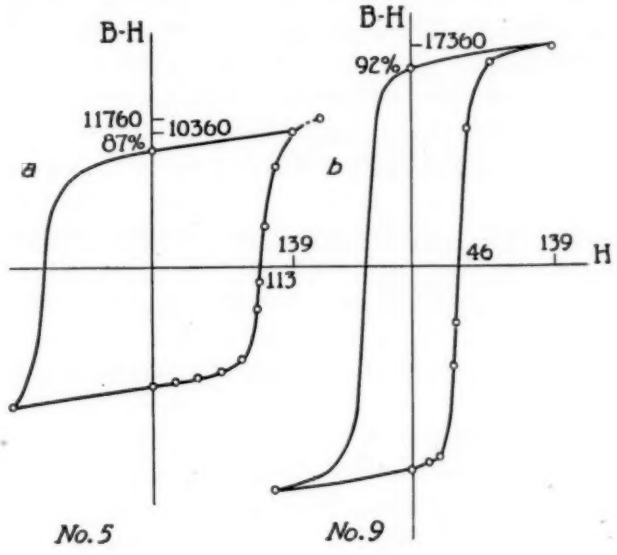

FIG. 2. Hysteresis curves for iron films.

The coercive forces of these films would indicate a thickness between 35 and 44 mμ as critical. However, the column of magnetic inductions

TABLE IV

Results for iron

δ is the film thickness in mμ; β_{139} and β_{167}, the magnetic induction at 139 and 167 gauss, respectively; I_r, retentivity in percent; H_c, coercive force in gauss

Film No.	δ	β_{139}	β_{167}	I_r	H_c	Film No.	δ	β_{139}	β_{167}	I_r	H_c
45	22	15,450	16,100	88	89	9	68	17,500	17,800	92	46
5	28.4	10,500	11,900	87	113	35	69	17,000	17,400	90	45
29	30	13,800	16,600	89	110	15	69.5	16,300	16,400	92	43.5
19	34	8,600	10,200	77	99	43	71.5	16,300	16,600	92	39
49	35	15,300	16,200	93	95	11	79	15,400	16,000	90	46
39	44	19,250	19,600	91	49	3	85	18,100	18,200	90	35
41	54	16,000	16,600	90	52	7	141	15,200	15,400	83	23
21	54	16,100	16,200	91	48						
47	59	13,700	14,100	90	69	Unannealed iron[5]		18,500	18,700	70	9

furnishes a valuable check on the correctness of the calculated thickness and indicates a slightly higher critical value. Film No. 39 is evidently of

[5] Ewing, J. A., "Magnetic Induction in Iron and Other Metals."

a greater thickness than the value calculated from weighting. Taking $\beta_{139}=16{,}000$ as the average magnetic induction of films of near the same thickness from which to calculate the thickness of No. 39, we obtain $\delta_{39}=52$ instead of 44. Similarly calculating the thickness of No. 47, we obtain $\delta_{47}=50$ instead of 59 mμ, which would make 50 mμ appear as the best value of critical thickness. These corrections indicate that the error in the thickness determination may be as much as 15 percent. But Table IV gives unmistakable evidence of a thickness critical for coercive force, placing its value at approximately 50 mμ.

The iron filament shows a strong tendency to oxidize even at pressures of .001 mm. The maintenance of evaporation then requires a progressively increased heating current, and at much higher pressures evaporation may not be accomplished. The study of the effect, if any, of pressure variation on the magnetic properties of the iron films would obviously require the use of oxygen-free gas. This was not attempted.

According to Ewing[5], the magnetic induction of bulk iron for the maximum fields used in this work should be about 18,700—(there is little difference in magnetic induction for annealed and unannealed iron at this field strength.) The magnetic induction obtained by the writer for evaporated iron films runs about 15 percent below this value. This does not agree with Sorensen's determinations which were of the order of 15 percent higher than that of bulk iron. The lower value would seem to be more in accord with the predictions of the Hall-effect in evaporated iron films[4,6] in that the low value of field required to saturate the Hall e.m.f. implies that a smaller intensity of magnetization is possible in such films than in bulk metal. It is possible, however, that the difference in magnetic nductions in the two investigations is due to dissimilar heat-treatments.

Summary of Results

This investigation of the magnetic properties of evaporated nickel and iron films was undertaken with the hope of determining the existence of a thickness critical for abrupt change in the coercive force, and of discovering the cause of certain peculiar hysteresis loop forms. Though difficulties arising frm ooccluded gases may have prevented the appearance of a critical thickness in nickel, surprising consequences of various types of heat-treatment are revealed. Nickel films deposited unheated have very narrow hysteresis loops, remarkable in that the magnetic induction is nearly proportional to the field up to 139 gauss.The magnetic induction at this field is from a third to a half that of unannealed nickel in bulk. If, however, the occluded gases are driven out by a pre-deposit heating, the

[6] Steinberg, Phys. Rev. **21**, 22 (1923).

magnetic induction, retentivity and coercive force all increase very decidedly giving magnetic properties very similar to those obtained on heating only during the deposition of the film. But if these heat treatments are combined, a large further increase in these properties is obtained, in which case the films are very hard mechanically as well as magnetically, and though magnetic fields in the evaporation apparatus were neutralized as far as possible, these films were all initially rather strongly magnetized.

In iron there is observed a thickness of about 50 mμ, which is critical for coercive force. This is approximately the value determined by Sorensen.[4]

The hysteresis loops for iron obtained in the two investigations both above and below the critical thickness are in agreement. Coercive forces and retentivities are numerically practically the same, but the present investigation gives values of magnetic induction which are about 30 percent lower than those of the earlier work.

Discussion

There is a definite effect of heating the film, namely an abnormally large hysteresis loop, and, at large fields, a more nearly normal susceptibility. There is much evidence that these effects are in some way related to the crystal formation. That the deposition of a metallic film on a cold surface is amorphous was first stated by Langmuir.[7] This theory has since had experimental verification with x-ray spectrograms[8] and with the ultra-microscope[9], while a post-deposit heating was found to induce a crystal growth. Ingersoll and DeVinney[10] found that sputtered nickel films deposited at liquid air temperature were practically non-magnetic. After being heated, these films assumed their usual magnetic properties. Though in no case were the films of the present investigation deposited at a really low temperature, the magnetic induction of the least heated films is very small even in the strongest fields available, and there is reason to believe that if deposition had occurred at very low temperatures, the films might be non-magnetic. The temperature required to induce crystal growth during deposition, if this is the cause in the change in magnetic properties, is decidedly less than that required after deposition has occurred.

There are some extraneous influences present whose effects might be considered as masking the intrinsic properties of the metal. That the

[7] Langmuir, Am. Chem. Soc. J. **38**, 2221 (1916).
[8] Kahler, Phys. Rev. **18**, 210 (1921).
[9] Reinders and Hamburger, K. Akad. Amsterdam Proc. **19**, 958 (1917).
[10] Ingersoll and DeVinney, Phys. Rev. **26**, 86 (1925).

effect of a pre-deposit heating of the foil is due to driving off the gas can scarcely be questioned. The fact that a film deposited *unheated* on a foil, which has been *previously heated*, has magnetic characteristics very similar to those of a film produced on a foil which is heated *during deposition only*, might infer that heating the foil either before or during deposition merely drives off the gas. But heating the film during its deposition produces the same change and of a similar magnitude whether or not the gas has been initially baked out of the foil. In either case the loop forms become more rather than less abnormal. It is evident, then, that the peculiar hysteresis loops cannot be due to the presence of gas. On the contrary, it seems that the gas, directly or indirectly, interferes with the phenomena.

We have assumed that the aluminum foil base on which deposition occurs does not affect the magnetic properties of the film. There are, however, two possible ways in which its influence might be present. The projected particles from the filament may alloy with the aluminum of the base. Were this true, the magnetic properties of the film would show decided change with thickness as the comparatively slow velocity with which the molecules emerge from the filament could not penetrate a depth of several hundred molecules of the aluminum. A second possible influence of the base is its interference with magnetostriction. Though this would not seem great enough to be the cause of the peculiar phenomena, experiments are now being devised in this laboratory in which all influences of the base will be removed.

One other operation deserves notice. When the film with its aluminum foil base is rolled for insertion into the magnetic test apparatus, a compression of the film must occur. For a film of thickness 100 mμ, on a foil of 1 mil thickness such as was used, rolled to a radius of curvature of 1mm which is approximately the minimum, this compression would amount to about one percent. Furthermore one side of the film is compressed slightly (about one percent) more than the other. Though the compression is much more than the elastic limit of the metals employed, since all films are similarly treated in this respect, it would not cause the remarkable variation observed in the film properties. However annealing after the rolling process should be tried.

It is well known that hysteresis decreases with increasing crystal size of metal in bulk. These crystals are probably very large as compared with those of evaporated films. It has been suggested that the function which determines hysteresis may be of a type that vanishes for either very large or very small crystals. Jensen[11] regards hysteresis as largely deter-

[11] Jensen, J. Am. Inst. Elec. Eng. **43**, 558 (1924).

mined by the amount of cementing material between the crystals which would ordinarily increase with decreasing size. It seems possible however that crystal strain or deformation may be a more important factor in determining hysteresis than mere crystal size. Perhaps perfect crystals are not formed by the evaporation process. The velocity of the particles on impinging may be too great for the molecular field properly to orient them. The observed film properties were not altered appreciably by changes in the velocity of emission, produced by variations of filament temperature. Welo and Baudisch[12] have produced crystals of magnetite by methods giving very different crystal sizes. Before they are annealed, their magnetic properties differ widely, but after annealing, even though crystal sizes remain dissimilar, their magnetic properties become similar. The necessity for annealing their crystals was probably occasioned by the rapidity of formation. It is possible that annealing the evaporated films would result in more nearly normal crystals.

McKeehan[13] considers atomic magnetostriction as the prime cause of hysteresis, and in the experimental work on which his conclusions were based, this view would seem to be correct. It would be remarkable indeed if all hysteresis could be traced to this one cause. The evidence obtained by this study of thin films indicates that hysteresis is a crystalline rather than an atomic phenomenon.

In conclusion the writer wishes to express his appreciation to the members of the Department of Physics of the State University of Iowa for their assistance and interest, and especially to Professor G. W. Stewart under whose direction the work was carried on.

HALL OF PHYSICS,
UNIVERSITY OF IOWA,
July 10, 1926.

[12] Welo and Baudisch in a private communication.
[13] McKeehan, Phys. Rev. **26**, 274 (1925).

THE HALL EFFECT IN BISMUTH WITH SMALL MAGNETIC FIELDS

By C. W. Heaps

Abstract

The Hall coefficient for a bismuth plate of dimensions 0.011×0.9×2.0 cm has been measured for magnetic fields ranging from 0.07 to 2.40 gauss. The average value of the Hall coefficient, R, in this range was 11.5, and variations of R due to change of field strength in this range were less than experimental errors. For larger fields the Hall coefficient of this specimen decreased from 13.5 for a field of 650 gauss to 5.9 for a field of 8600. It is concluded that for similar ranges of field the data reported by Palmer H. Craig are erroneous, probably because of insulation leakage or uncompensated thermomagnetic effects. A simple method of making very thin bismuth plates is described.

Introduction

IT IS a well known fact that the coefficient of the Hall effect for ordinary cast bismuth increases as the magnetic field is diminished.[1] Recently Palmer H. Craig has reported[2] surprisingly large values of this Hall coefficient when magnetic fields smaller than about 0.3 gauss were used, and he suggests that modifications will have to be made in the theory of the Hall effect in order to account for his results. There are already several other phenomena connected with the Hall effect which theories have not explained; the genuineness of this new phenomenon should therefore be very thoroughly established.

The writer on several occasions has measured very small electromotive forces produced by the Hall method and has experienced some difficulties because of insulation leakage in various parts of the circuit. This leakage, if it exists, will usually result in a specious magnification of the Hall constant. Another difficulty sometimes arises if thermoelectric currents have to be balanced out of the Hall circuit. The Joule heat of the primary current must be dissipated in the specimen, and it is very difficult to secure uniform temperature under these conditions. Convection currents and irregularities of structure of the specimen are apt to produce slight temperature differences, and these result in thermal e.m.f.'s when associated with contacts used for detecting the Hall e.m.f. Such thermal e.m.f.'s may be balanced out by the potentiometer when no magnetic field acts. Putting on the field, however, will destroy this balance, since the thermoelectromotive force of bismuth with respect to copper is altered by the presence of a field.

[1] Campbell, "Galvanomagnetic and Thermomagnetic Effects," p. 42.

[2] Craig, Phys. Rev. 27, 772 (1926).

The result might be an apparent exaggeration of the Hall e.m.f. To detect such an effect the primary current must be broken and the effect of a magnetic field on the potentiometer setting noted before there is time for equalization of temperature in the specimen.

To eliminate errors of this kind it is often sufficient to reverse the direction of the magnetic field and calculate the mean of the Hall e.m.f.'s for the two directions of field. The thermal effect is thus averaged out, since it does not reverse with the field while the Hall e.m.f. does.

Craig appears to have been very careful about mounting his specimen but does not mention any special precautions taken to keep his electrical circuits insulated from each other. Also, he states that "potentials due to Thomson and allied effects were accurately measured the instant the longitudinal current was broken,"—however, he apparently did not test for the effect of the field on these potentials. Furthermore, it does not appear in his paper that spurious temperature effects were averaged out by reversing the magnetic field.

Because of the possibility of these sources of error in Craig's work the writer has made some measurements of the Hall coefficient in weak magnetic fields and has not found the abnormal values reported by Craig.

Apparatus

A thin plate of bismuth (listed by Eimer and Amend as c.p.) was made by the following method. A glass tube with one end drawn down slightly was clamped vertically and a bismuth rod inserted. The rod was prevented from slipping out of the bottom by the slight constriction there. About 10 cm below the end of the tube was placed a clean, horizontal glass plate. The lower end of the glass tube was now heated with a small flame till the bismuth melted and a single large drop was allowed to fall on the glass plate below. By a little practice in adjusting temperatures and distance of fall very thin, uniform, circular films of metal can be produced on the glass plate in this way.

The film chosen for experimentation was 0.011 cm thick, and was cut into a rectangular shape of dimensions 0.9×2.0 cm. Small arms of bismuth were left projecting from the sides of the specimen and the terminals for the Hall e.m.f. were soldered to the ends of these arms with Wood's metal. The leads for the primary current were soldered to strips of sheet copper which in turn were fixed with Wood's metal to the bismuth specimen.

Manipulation of the plate was not difficult because it was rather tightly adherent to the glass upon which it was formed. Hence, it was

possible by carefully scraping the edge of the plate to adjust the Hall electrodes so that they were quite accurately on an equipotential surface when the primary current flowed and there was no magnetic field.

For the sake of thermal insulation a thick coat of paraffin was put over the plate and over the junctions of all wires leading to it, and a layer of cotton was wrapped around the whole assembly. It was then mounted, with ebonite insulation, on a stand arranged with a graduated circle so that the specimen could be rotated about a horizontal axis in the plane of the plate and parallel to its length.

The Hall electrodes were connected through a potentiometer to a galvanometer of resistance 16.6 ohms and sensitivity 17.3 mm per microvolt. The primary current electrodes were connected through an ammeter and rheostat to a 6-volt storage cell. The galvanometer circuit and the primary current circuit were insulated from the earth and from each other by ebonite,—except, of course, where interconnection occurred in the bismuth plate.

When a primary current of 1.3 amperes was sent through the specimen it required about half an hour to secure constant temperature conditions. After that length of time the galvanometer reading remained quite constant, or drifted so slowly as not to interfere with observations.

For producing the magnetic field a pair of Helmholtz coils was used. Each coil had a radius of 10.2 cm and consisted of 5 turns of No. 24 enamelled wire on a carefully turned micarta form. The field for a given current was calculated from the dimensions of the coils. The effect of the earth's field was eliminated as in Craig's work, by setting the plane of the bismuth plate parallel to the earth's field.

Measurements were made as follows. The galvanometer readings were noted in quick succession for the field in one direction, for the field reversed, and for the field in the original direction. The reading for the reversed field was subtracted from the average of the first and third readings and the difference divided by two. The result gave the deflection due to the Hall effect for the field used, and errors due to slow drift of the galvanometer were eliminated. The corresponding e.m.f. was calculated from the known sensitivity of the instrument. This method is quick and accurate, and it gives the same result as the potentiometer method provided the potential drop in the specimen due to the galvanometer current is negligible compared with the Hall e.m.f. [3]

[3] Heaps, Phys. Rev. 12, 346 (1918).

The potentiometer in the galvanometer circuit was used for balancing small thermal e.m.f.'s and for obtaining the sensitivity of the galvanometer.

The sensitiveness of the apparatus was such that turning the plate over so as to reverse the earth's field gave a deflection of 24 mm.

RESULTS

The table gives a set of results obtained for small magnetic fields.

TABLE I

The Hall coefficient for bismuth for small fields, with a primary current of 1.3 amps.

H (gauss) :	0.07	0.09	0.13	0.23	0.29	0.35	0.40	0.51	0.77	1.06	1.54	2.40
R :	11.4	11.3	11.0	11.3	11.3	11.8	11.5	11.7	11.9	11.6	11.6	11.7

Here H is the magnetic field strength and R is the Hall coefficient calculated in the usual way. Each value of R recorded above is the average of at least five values. These five values for any one field differed among themselves by about as much as the different values of R in the table. Apparently the change of R for a range of magnetic field from 2.4 to 0.07 gauss is no greater than the errors of the experiment. Craig found R increasing by a factor of more than 10 in this same range.

To test the effect of electric leaks one side of the potentiometer was connected by a wire to the slate bench on which the apparatus was disposed. Craig states that such a connection in his apparatus was found to increase stability, so presumably he used it in his work. It introduces a leak to ground in the galvanometer circuit. Another wire was next used to connect the enamelled iron tube of the rheostat in the primary current circuit to the floating side of the reversing switch in the circuit of the Helmholtz coils. No particular care had been taken to insulate these coils from the slate table top, and the 6-volt storage battery used for exciting the coils was standing directly on the tile floor supporting the table. This second wire thus served as a leak from the primary current circuit to ground, and the effectiveness of the leak was altered by closing the reversing switch.

With these leaks in operation and a current in the coils to give a field of 0.06 gauss, the galvanometer deflections were 4.1 and 2.0 cm, respectively, for the two settings of the reversing switch. The smaller of these deflections gives an apparent Hall coefficient about 17 times too large for this field. When larger magnetic fields were used the effect of these leaks was not so apparent because the deflections which they produced were in this case smaller than the deflections due to the Hall e.m.f.

The curve of Fig. 1 shows how the Hall coefficient of this particular specimen varies for strong magnetic fields. These fields were produced by a Weiss electromagnet with pole pieces 10 cm in diameter and 2.3 cm apart. The fields were measured with a bismuth spiral. There is no evidence of a rise in the curve as the field increases, though Craig found R increasing from 15 to 29 as the field increased from 1000 to 4220.

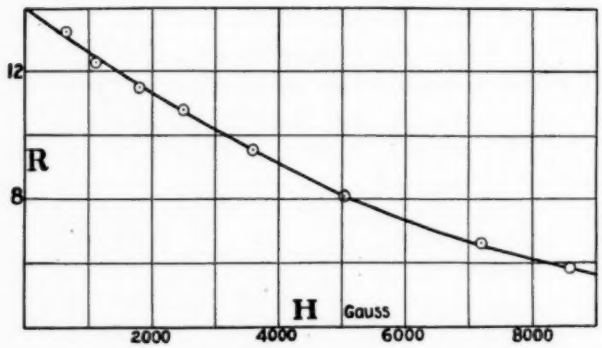

Fig. 1. Variation of the Hall coefficient, R, with the field strength, H.

The curve of Fig. 1 indicates a larger value of R for small fields than the data of Table I show. This apparent discrepancy is due to the fact that a primary current of only 0.2 amperes was used in getting the curve, while 1.3 amperes were used for the data of the table. The larger current heated the thin bismuth plate very perceptibly and the resulting rise of temperature diminished the Hall coefficient.[4]

Conclusions

For bismuth in the form of a crystal conglomerate the Hall coefficient diminishes in regular fashion as the magnetic field increases. There is no abnormal increase of the coefficient as the field becomes very small.

It appears probable that Craig's results are incorrect because of imperfect insulation of his apparatus. He states that the stability of his system was increased by grounding his potentiometer. There should, however, be no instability which could be corrected in this fashion unless leaks of variable resistance are present.

It is also possible that the lack of agreement of Craig's results with those reported in the present paper is due to his not having eliminated thermomagnetic effects.

The Rice Institute,
Houston, Texas,
October 18, 1926.

[4] Campbell, "Galvanomagnetic and Thermomagnetic Effects," p. 49.

TEMPERATURE DISTRIBUTION ALONG A FILAMENT

By V. Bush and King E. Gould

Abstract

A method has been developed for adapting a new integrating machine to the solution of: (1) the integral equation which applies to the distribution of thermionic emission along the central portion of a long filament in an evacuated vessel, the effect of the thermionic emission upon the filament temperature (by changing the heating current as well as by a direct cooling action) being considered; (2) the differential equation which applies to the temperature distribution near the end of a long filament from which the thermionic emission is negligible compared with the filament heating current; (3) The integro-differential equation which applies to the distribution of temperature and thermionic emission along an entire filament heated, in an evacuated vessel, by a direct current. This takes into account the effects of thermionic emission as well as cooling due to thermal conduction. All these solutions fully account for the variation of the following quantities with temperature, graphical relations being used throughout: (a) thermal conductivity; (b) thermionic emission; (c) resistivity; (d) radiation. The method has been applied to various typical cases of tungsten and thoriated tungsten filaments, and in those cases where an experimental check was possible it was found that the results were in good agreement with the measured quantities.

Introduction

THE differential equations which represent physical conditions along an incandescent filament heated by a direct current may be set up easily, and, with certain simplifying assumptions, solved by formal methods. Even with these simplifying assumptions, such solutions become very laborious, and when the empirically determined variations of the parameters are to be taken into account, such formal solutions become impossible.

There has been developed, in the Massachusetts Institute of Technology Electrical Engineering Research Laboratory, an integrating machine which may be adapted to the solution of numerous types of differential and integral equations, and the equations which apply to the incandescent filament are among these. The integral equation which applies to the part of an electrically heated, thermionically emitting filament over which the cooling due to the thermal conductivity of the filament is small may be solved directly upon this machine. Furthermore, by a method of successive approximations, the integro-differential equation which takes into account the thermionic current as well as cooling by thermal conduction to the filament supports may

be solved by means of this new device. In every case the actual resistivity, thermal conductivity, radiation emissivity, and thermionic emission, as functions of the temperature, are considered; graphical, rather than analytical relations being used throughout.

The object of this paper is to show the method of attack upon this filament problem, to present some of the typical results obtained, comparing them with measured quantities, and to bring together in a single check various empirically determined properties of tungsten and thoriated-tungsten filaments.

Equations Which Express Physical Conditions

No cooling due to thermal conduction. Consider the central portion of a long filament heated by a direct current, and let the filament be emitting thermionically at such a rate that the total emission over the portion considered is great enough to affect the filament current, all emitted electrons being drawn from the wire to a neighboring plate by an electric field. The emission is sometimes comparable with the filament current in the case of thoriated-tungsten or oxide-coated filaments, or with filaments in alkali vapor. Let it be assumed that the cooling due to thermal conductivity is negligible over this part of the filament, as it will be if the filament is very long. The following identity applies to any element in this portion of the filament;

Electrical Input = Radiation output + Cooling due to thermionic emission. Or,

$$i^2 R_T = f(T) + \phi I \tag{1}$$

where i is the filament current, which is a function of the distance along the filament (considered throughout this paper as measured from the negative end of the portion of filament); R_T is the resistance of the filament per unit length, as a function of the absolute temperature, T; $f(T)$ is the radiation per unit length of filament at the temperature T, and ϕI is the cooling per unit length of filament due to the thermionic emission, I, at the temperature T, ϕ being the work function for the filament material in equivalent volts.

If i_0 represents the filament current at the negative end of the portion of filament considered, then i is given by

$$i = i_0 - \int_0^x I dx \tag{2}$$

and thus Eq. (1) becomes

$$i_0 - [(f(T) + \phi I)/R_T]^{1/2} = \int_0^x I dx \tag{3}$$

which may be written in the form

$$\psi(T) = \int_0^x F(T)dx \tag{4}$$

Emission neglected. If the filament is such that the emission current is negligible compared with the filament current, then the filament current, i, remains constant along the wire, as is the case usually with pure tungsten filaments. In this case the cooling due to thermionic emission is usually entirely negligible. Taking the cooling due to thermal conductivity into account,

Electrical input = Radiation output + Conduction output, or

$$i^2R_T = f(T) + \left[- K_T\frac{d^2T}{dx^2} - \frac{dK_T}{dT}\left(\frac{dT}{dx}\right)^2 \right] \tag{5}$$

where K_T is the thermal conductivity of the filament per unit length, at the temperature T, x is the distance from a support, and the other symbols have the same meaning as before.

In one case (Fig. 7), the second conduction term in the square brackets of Eq. (5) was neglected. There is no loss of generality of the method in doing this, as a new temperature scale, T', may be adopted with which the conduction output will be given by one term only, $[-Kd^2T'/dx^2]$, K in this case being constant. This will be demonstrated below. After making this substitution we may write

$$d^2T'/dx^2 = (1/K)[f(T) - i^2R_T] = \lambda(T) = \lambda'(T'). \tag{6}$$

Emission and thermal conductivity both accounted for. If the emission is sufficient, and enough of the emitted electrons are removed by an electric field, the filament current is appreciably affected. Assuming that all emitted electrons are removed, the equation which represents conditions along the filament is,

$$i^2R_T = f(T) - K(d^2T'/dx^2) + \phi I \tag{7}$$

the temperature scale which makes the thermal conductivity constant being adopted. x here represents the distance from the support at the negative end of the filament.

Eq. (7) may be written

$$\left[i_0 - \int_0^x Idx \right]^2 R_T = f(T) - K(d^2T'/dx^2) + \phi I \tag{8}$$

or

$$(f(T) - Kd^2T'/dx^2 + \phi I)/R_T]^{1/2} = \int_0^x Idx \tag{9}$$

Temperature scale to give constant thermal conductivity. In terms of degrees absolute, the conduction output per unit length of filament is given by the bracketed expression in Eq. (5). But in terms of the new temperature scale T', this is assumed to be $[-Kd^2T'/dx^2]$ where K is an arbitrary constant. Thus

$$K_T(d^2T/dx^2) + (dK_T/dT)(dT/dx)^2 = K(d^2T'/dx^2) \qquad (10)$$

This has the solution

$$T' = (1/K)\int_0^T K_T\, dT + K_0 \qquad (11)$$

which gives the relation between T' and T, K_0 being a second arbitrary constant. Any value of K and K_0 may be assumed; the final result in terms of T will be the same in any case.[1]

Solution of Equations

In solving the differential and integral equations, the values of resistivity, thermal conductivity, and radiation intensity of tungsten, as functions of the temperature, were taken from a paper by Forsythe and Worthing,[2] while the thermionic emission from tungsten and thoriated tungsten, as a function of the temperature, and the work function for thorium were taken from a paper by Dushman.[3] For lack of better knowledge, the thermal conductivity has been assumed constant up to 1000°K, and equal to its value at that temperature, the variation above this temperature being taken into account.

Eq. (5) may be solved directly upon the integrating machine, to give the thermionic emission per unit length, against distance from any given point on the filament. This solution, as has been noted, neglects all effects due to thermal conductivity. It is particularly fortunate that the emission can be directly determined, as it is the emission that is wanted, more often than not, in such a problem, and if the temperature distribution is desired it may readily and accurately be obtained from the emission curve.

Fig. 1 shows a typical result obtained by this method. This is drawn for a thoriated tungsten filament three mils in diameter carrying 0.976

[1] A description of the integrating machine and its use in evaluating such integrals as that of Eq. (11) will be found in the Jour. Frank. Inst. Jan. 1927. The adaptation of this machine to the solution of equations such as (5), and (8), is not included in that paper, but the authors of the present paper hope to publish an article on that subject in the near future.

[2] Forsythe and Worthing, Astrophys. J. **61**, 147 (1925).

[3] Dushman, Gen. Elec. Rev. March 1923.

amperes at the point from which the distance is measured (which is the negative end of the portion of filament considered), and it is assumed

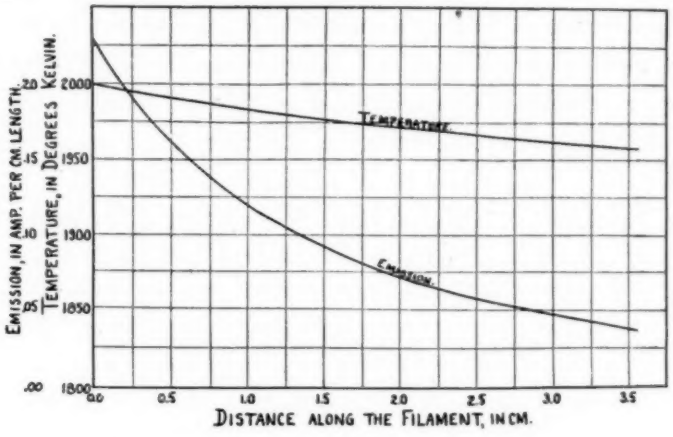

Fig. 1. Variation of temperature and thermionic emission along a thoriated tungsten filament, diam. 3 mils, current 0.976 amps.

that all emitted electrons are carried away to an adjacent plate by an electric field.

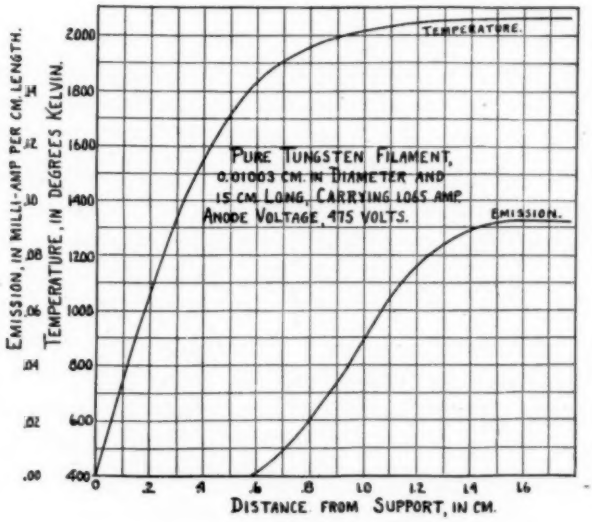

Fig. 2. Solution of Eq. (6) neglecting the cooling term.

Fig. 2 represents the solution of Eq. (6), using the absolute temperature scale, with a variable thermal conductivity, but neglecting the second cooling term. The boundary conditions were: at $x=0$, $T=$

400°K, and when $i^2R_T = f(T)$, $dT/dx = 0$. The latter assumption is equivalent to saying that the filament was so long that the temperature at the center became that of a similar filament infinitely long. This is practically the case. As the filament was of pure tungsten, the thermionic emission had virtually no effect upon the temperature distribution.

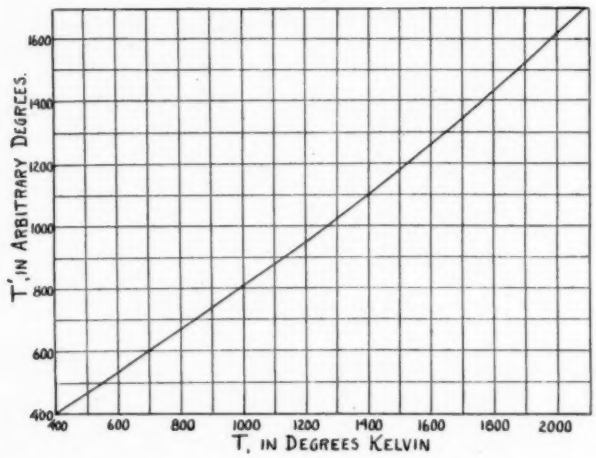

Fig. 3. Relation of the temperature scale T' for which the thermo-conductivity of tungsten is constant to the absolute temperature scale, T.

Fig. 3 shows the relation of the temperature scale T', for which the thermal conductivity of tungsten is constant, and equal to 1.23 watts per cc per degree C, to the absolute temperature scale T, and represents a solution of Eq. (11). Fig. 3 was obtained by integrating, with the integrating machine, the thermal conductivity, K_T, plotted against the absolute temperature, K being chosen to give a convenient scale for T', and K_0 being such as to make the two scales coincide at 400°, that is,

$$T' = (1/K)\int_{400}^{T} K_T\, dT + 400$$

Fig. 4 represents the solution of Eq. (8), using the temperature scale T', for the filament of Fig. 2, under similar conditions. Thus Fig. 4 should give the correct temperature distribution, rather than Fig. 2, which is only an approximation. However, a comparison of Figs. 2 and 4 will show that the effect of neglecting the second cooling term is, in this case at least, very small indeed.

The data for the filament to which Figs. 2 and 4, as well as Fig. 5, apply were taken from a paper by Dushman, Rowe, Ewald, and Kidner[4] (Tube 107–1). The calculated values check quite well with

[4] Dushman, Rowe, Ewald and Kidner, Phys. Rev. March, 1925.

the measured quantities, as will be seen from the data in Table I. Fig. 5 is just the same as Fig. 4, except that it is drawn for a smaller filament current, and was determined as a further check of the method, and also of the data in the paper noted above.

TABLE I

Data for the filaments referred to in Figs. 2, 4 and 5.
The quantity f is the ratio of emission which would exist if the entire filament were at maximum temperature to the actual total emission.

	Fig. 2		Fig. 4		Fig. 5	
	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.
Filament voltage (volts):	11.99	11.77	12.02	11.77	9.32	9.12
Maximum temperature (°K):	2070	2065	2070	2065	1900	1897
Total emission (m.a.):	1.21	1.15	1.21	1.15	.110	.1065
f:	1.147	1.143	1.147	1.143	1.18	1.167

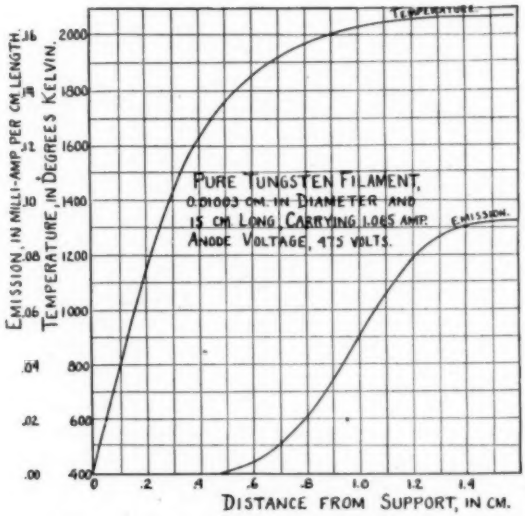

Fig. 4. Solution of Eq. (8) using the temperature scale, T'.

Fig. 6, which is drawn for a thoriated tungsten filament with zero potential gradient at the cathode (that is, with an electric field just great enough to remove all emitted electrons), represents the solution of Eq. (8), with the boundary conditions; when $x=0$, $T=400°K$, when $x=$length of filament, $T=400°K$, and the assumption that over the central part of the filament there was no cooling due to thermal conductivity. This cooling was found to be negligible in the actual case. It will be noted that the emission falls off very rapidly as the distance from the negative end of the filament increases, because of the drop in filament temperature produced by the decrease of filament current.

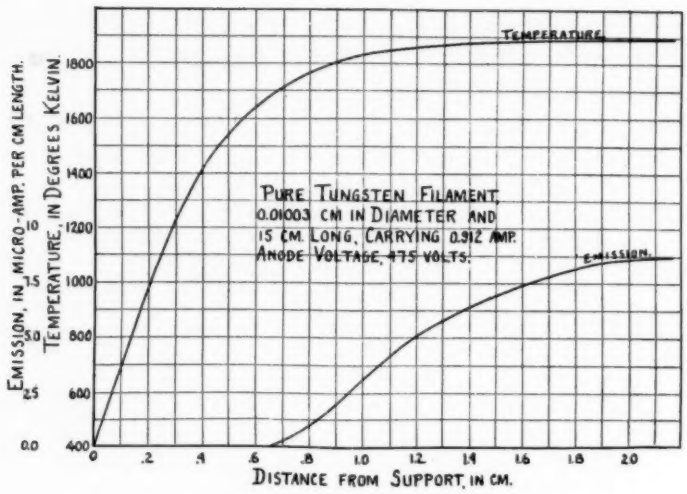

Fig. 5. Solution of Eq. (8) using the temperature scale, T^{ν}. The filament current is less than for Fig. 4.

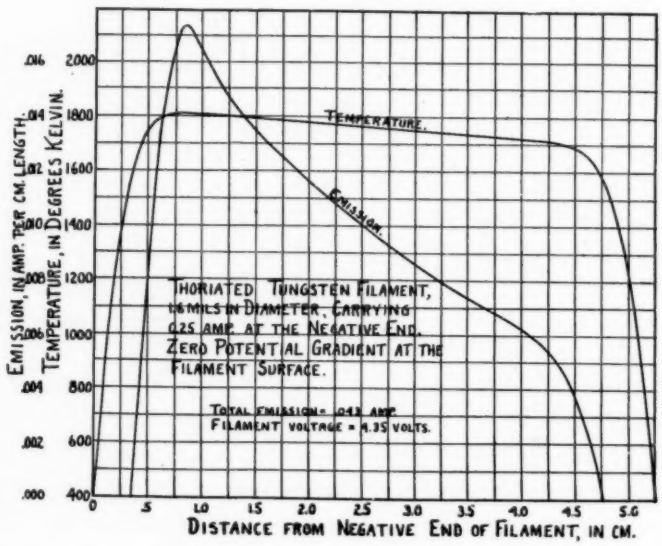
TEMPERATURE
EMISSION
THORIATED TUNGSTEN FILAMENT,
1.6 MILS IN DIAMETER, CARRYING
0.25 AMP. AT THE NEGATIVE END.
ZERO POTENTIAL GRADIENT AT THE
FILAMENT SURFACE.
TOTAL EMISSION = 0.43 AMP.
FILAMENT VOLTAGE = 9.35 VOLTS.
EMISSION, IN AMP. PER CM. LENGTH.
TEMPERATURE, IN DEGREES KELVIN.
DISTANCE FROM NEGATIVE END OF FILAMENT, IN CM.

Fig. 6. Solution of Eq. (11) assuming the temperature to be 400°K at the ends of the filament.

Fig. 7 shows that the cooling due to thermionic emission from the thoriated tungsten filament is considerable, the error in maximum temperature which would result if this cooling term were neglected being about 125°K. Fig. 7 also gives some idea of the effect of other terms in Eq. (8), and shows the several steps in obtaining the temperature distribution of Fig. 6 from $x=0$ to the point where dT/dx is 0. First the filament current was assumed constant, and curve (4) was determined. The second cooling term was neglected here, but the effect

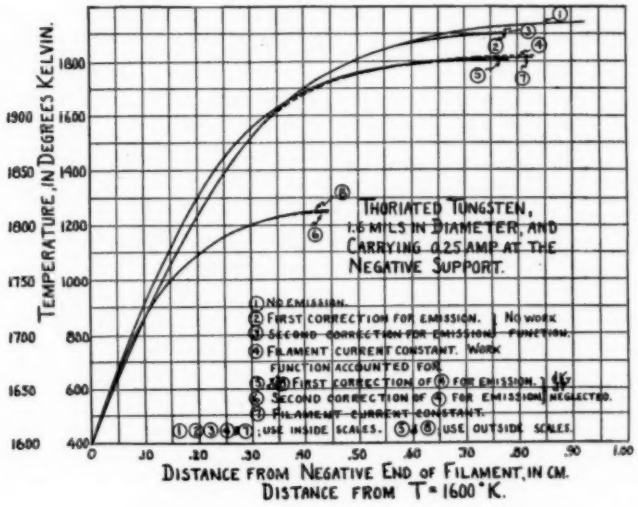

Fig. 7.

is very small, as a comparison of curves (7) and (4) will show. Then the value of $\int_0^x Idx$, as a function of x, was determined from curve (4), and placed in Eq. (8) which was solved, as before, for curve (5). Curve (6) was obtained from (5) in a similar manner, and as these last two were practically coincident, the maximum difference being about 2°K, the successive approximations were carried no further. The central portion of the emission curve of Fig.6 represents the solution of Eq. (3), and the temperature distribution near the positive end of the filament was determined just as for the negative end.

A Fellowship from the Çoffin Foundation made possible the pursuance of this work.

ELECTRICAL ENGINEERING RESEARCH LABORATORIES.
MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
April, 1926.

BOOK REVIEWS

Handbuch der Physik. Edited by H. GEIGER UND KARL SCHEEL. Band I, *Geschichte der Physik*. Vorlesungstechnik.—The first 179 pages of this volume is a history of physics from antiquity down to the year 1895, from the pen of E. Hoppe of Göttingen. The history is prepared largely from original sources or from recent articles and monographs on special historic topics. It is rich in bibliographical references. That antiquarian research is bringing to light matters of interest to physicists is evident from the fact that Hoppe devotes three pages to Babylonian developments in arithmetic, astronomy and metrology. The author makes out a case in favor of a Babylonian "absolute system" of units. Time was measured by sun-dials and also by water clocks. The unit of weight (mine) was the amount of water escaping in a unit of time (sussu) from an opening at the bottom of a vessel kept full of water. Thus, it is suggested that the Babylonian yard, mine, sussu corresponded to our C G S-system. The author is quite free from national bias. Attributing the electric telegraph to Gauss and Weber, and failing to mention Joseph Henry whose Albany experiments came somewhat earlier, is only an oversight. The treatment of the history of the nineteenth century is necessarily condensed and is not without gaps. But all things considered, this outline history of physics deserves commendation.—Pp. 404. Julius Springer, Berlin, 1926. FLORIAN CAJORI

Anregung von Quantenspruengen durch Stoesse. J. FRANCK and P. JORDAN.—The experiments of Franck and Hertz in 1913 opened up a new field in experimental physics—the study of the dynamics of the interactions between electrons, atomic structures, and radiation. This study, in which the senior author of the present book has played a leading role, has been guided by the quantum theory of atomic structure which has recently been put in a powerful form by Heisenberg, Born and Jordan. The authorship of the present book therefore assures the reader of an unusually competent exposition of the experimental facts and of their theoretical interpretation.

The somewhat one-sided development of the subject is reflected in the book. The chapters dealing with the measurements of critical potentials and their relation to spectroscopic data show the very satisfactory completeness of our knowledge of the energy relations at impact, at least with atoms. On the other hand the chapters on the kinetics of the electron in gases, on the efficiency of excitation by electron impact, on ionization and excitation by positive ion impact indicate how very meagre is our knowledge of the momentum changes at impact, and the conditions, other than energetic, which determine whether or not a collision will result in an excitation of the atom structure. The last chapter contains a very interesting discussion of the possibilities of applying the method of impacts to the study of the elementary processes of chemical reactions.

The book is of great value not only for its complete, concise and logical presentation of the facts (the literature references are complete up to the first months of 1926) but also for the many stimulating suggestions of ways for the further development of the fascinating subjects under discussion.—Pp. viii + 312. 51 figs. Julius Springer, Berlin, 1926. JOHN T. TATE

Introduction to Contemporary Physics. KARL K. DARROW.—New as the science of subatomic physics is, the motives for its study are among our oldest forms of scientific interest, dating back at least to the time when fundamental questions of the origin and nature of the material universe were given the very different answers still accepted by the self-styled Fundamentalists. Modern answers to these fundamental questions differ from the ancient answers not merely in content, nor merely in emphasis on the descriptive rather than the historical aspects of the questions. The ancient authors wrote with a self-confidence most complete and contagious, and usually stated results without any discussion of evidence; the contemporary physicist, on the other hand, lacks

the self-confidence, and asks his readers, or such of them as can, to study the evidence and judge for themselves the validity of his answers. This demands of contemporary intelligent readers a willingness to study a great mass of experimental data, most of which would be quite uninteresting, not to say boresome, to the majority of them, were it not related to these fundamental questions. To an author of a book on contemporary physics, this situation presents a serious problem. Relating these dry data to the live questions means, practically, relating the data to theories, tentative answers to the questions. The problem is, to establish this relation without allowing it to give the theories a false air of authority. In the words of the author, "The only feasible procedure is to separate the data from the models, as far as is reasonably practicable; to choose a few theories for presentation, according to one's own fallible estimate of their serviceableness, elegance, or chance of long survival; and to advise the reader to discriminate between the facts of experience and the atom-models devised to copy them, and in dealing with these latter to distinguish their essential from their irrelevant features. This advice I have tried to give in the introductory pages, and at intervals elsewhere."

The author's execution of this procedure commands most hearty admiration. In his Prolegomena, the relation of theories to experimental data is discussed with a clarity and perspective giving invaluable guidance to the student venturing for the first time into serious exploration beyond the settled ground of classical physics. If, as is possible, the author's caution might lead the beginner to despair of getting answers to fundamental questions bearing a closer relation to reality—whatever that is—than is suggested by the word "model", such doubts are dispelled in the first two chapters, entitled "The Experimental Electron" and "The Experimental Atom", where the basic facts about these once-hypothetical particles are established. In the next chapter evidence is amassed, leading to the subdivision of electrons within the atom into three groups, those concerned in properties of atoms showing periodicity in the series of elements, those showing steady progression, and those showing neither; these groups are then identified as outer, inner, and nuclear groups. The positive electricity is next located, by reference to alpha-ray data, and the data from deflections of electrons by atoms is used to show the ambiguous character of the term "radius of an atom". The main features of the picture of the atom are thus derived from experimental evidence, with a minimum of reference to any theories.

When radiation is taken up, the spectacular history of the wave and quantum theories brings theoretical speculation into more prominence. Nevertheless, the existence of stationary states of electrons in atoms is deduced from experimental evidence before these states are described as orbits; and in the seven chapters devoted to them, the properties of these states are treated in the same way as far as appears practicable. The historical order of the theoretical and experimental work is not overlooked, but is discussed in such a way as to make it subordinate to this logical arrangement. This policy of maintaining so thoroughly the distinction between the established and the tentative aspects of the theories necessarily involves a good deal of repetition and extra work, on the part of the student, as well as the author, but it insures the student's flexibility of mind with regard to the tentative aspects—that is, with regard to a very large fraction of the subject—and after all, is not such a valuable result well worth a good deal of work?

While this book is obviously intended for students with sufficient interest and intelligence for real work, it does not presuppose a knowledge of physics beyond a two or three quarters college course, nor of mathematics beyond elementary calculus. This, of course, limits its scope somewhat. The correspondence principle, for example, gets very scanty recognition. But this limitation makes the book available not only for prospective physicists, but for chemists, biologists and others willing to work for a clear idea of the basis for the contemporary physicists' views of matter. From the reviewer's experience with many reports in independent reading by such students, it is evident that this book will prove extremely useful.

Among its valuable features, in addition to those mentioned above, is its excellent style. It makes evident to the reader that he must not be in the class for whom a current periodical abbreviates "Continued on next page" to "Just turn the page", but not to "Over"; nevertheless it is straightforward, clear and human. This last quality is especially noteworthy in a book on this subject, where each grade of readers requires its own proper medium between cold, plain, uniform, matter-of-fact statements, that can be read in a monotone, and the "popular", animated and animistic, Sunday-supplement style, that acquaints its readers with difficulties of the helium-atom problem through extensive case studies on bigamous households. In this book, matter-of-fact exposition of course fills most of the pages, but it is in a style far from cold or plain, and it is relieved by other material which, as in the Sunday supplement, is suitable for the class of readers for whom it is written. Thus facts lending themselves readily to quizzical expression are enlivened thereby, and on the philosophy of scientific theorizing, a topic at once fundamental, abstract, and easily lost in dullness, the vivacity of many of the comments on its psychological aspects helps the student to realize that the discovery of the laws of things so far removed from human experience is an intricate and fascinating human problem.—Pp. xxvi & 453. D. Van Nostrand Co., 1926. Price $6.00.

D. L. WEBSTER

Magnetism and Atomic Structure. EDMUND C. STONER.—This book of 371 pages with 56 diagrams includes the most important advances in our knowledge of magnetism through the year 1925. It discusses magnetism in the light of the Bohr theory of atomic structure. It does not pretend to be exhaustive. However, the important facts and theories are presented concisely and lucidly. The style is clear and attractive. Experimental methods used in determining magnetic constants are described in sufficient detail. It is written by an investigator and an expert.

Some of the subjects treated are: The history of the subject, classical electromagnetic theory, quantum theory, the gyromagnetic effect, Gerlach and Stern experiments, the Zeeman effect, the Barkhausen effect, the assignment of electrons to orbits and interpretation of magneton numbers, the theory of Weiss, relation of magnetism to chemistry, and resonance radiation.

It is of particular interest to see Stoner's view on the reasons for the particular assignment of electrons to orbits which is due to him. To the reviewer, however, it would appear that the intensities of x-ray lines are not as conclusive proofs as the general consistency of the Goudsmit, Pauli, Heisenberg, Hund, Russell, Laporte spectroscopic developments which are also mentioned in the book.

The realization of the importance of the spinning electron came after the book was written. The gyromagnetic anomaly, g values, and the relativity doublet difficulty appear now in a new light, especially with the aid of the new mechanics. Similarly the subject of resonance radiation has received recent important contributions which could not be included. Among older papers it may be mentioned that Fermi and Rasetti have performed the same experiment as Breit and Ellett in a more thorough manner and quite independently.

Various interesting suggestions are made throughout the book. For example, it is suggested that Gaschler's experiments and the high magnetic field (10^{11} gauss) due to K electrons in U are connected with each other.—Pp. xiii + 371, 56 figs., Methuen and Co., London, 1926.

G. BREIT

Kolloidchemie. RAPHAEL ED. LIESEGANG.—This volume forms Volume VI of Wissenschaftliche Forchungsberichte, Naturwissenschaftliche Reihe, Edited by Dr. Raphael Ed. Liesegang. It is in reality a collection of notes and references to the colloid chemical literature which has appeared since 1914. The author states in the preface that the volume is not to be regarded as a textbook or as a handbook but rather as a "Sammelreferate". The book is divided into 24 sections or chapters including such

headings as synthesis, optics, viscosity, plasticity, capillarity, adsorption, contact catalysis, coagulation, sedimentation, electrical phenomena, Brownian movement, surface tension, etc., and some 800 literature citations are given.

Probably no other colloid chemist, given the task of selecting the most important contributions to the literature of colloid chemistry since 1914, would select the same group which has been selected by Liesegang. It is probably equally true that no two colloid chemists would select groups that closely approximated each other, consequently the reviewer cannot find fault with the selection of material. That is the prerogative of the author, and it is only natural that the selection should reflect his views. The reviewer, however, does not believe that the relatively few references to American and English literature as contrasted to the many citations to German literature is a fair index of the number of meritorious publications. Another valid criticism is the brief treatment of certain sections; for example, the "viscosity of protoplasm" is given 9 lines with 2 citations, both to German literature, and "plasticity" is given less than a page with only 4 references, all to German literature. How the author could overlook the contributions of Bingham in this field is beyond the comprehension of the reviewer.

The volume contains no tabular data or figures, and its value will be limited to the use which the physicist or chemist can make of it as a source of collected and annotated literature citations. It is well printed on good paper and appears relatively free from typographical errors; however, the dibenzoyl-l-leucine mentioned near the top of p. 131 should be di-benzoyl-l-cystine. It should be in all reference libraries.—Pp. xii + 176. Theodor Steinkopff, Dresden and Leipzig, 1926. Price 8.0 M unbound, 9.5 M bound.

ROSS AIKEN GORTNER

The Anatomy of Science. GILBERT N. LEWIS.—This book, which comprises the Silliman lectures at Yale for 1926, is ostensibly addressed to the intelligent layman, and presents to him an account of the contemporaneous attitude of scientific men toward our fundamental scientific notions. The chapter headings show the scope of the book: Methods of Science—Numbers; Space and Geometry; Time and Motion; Light and the Quantum; Probability and Entropy; The Non-Mathematical Sciences; Life—Body and Mind.

In spite of its ostensible address to the layman, the physicist will perhaps find even more of stimulation and interest here than the layman. Every physicist is becoming increasingly aware that one of the most important tasks both for him as an individual and for physics as a science is a reformulation of attitude toward fundamental concepts. The author has been known for his interest in fundamentals ever since he was one of the first in this country to accept the then new doctrine of relativity, and now his matured attitude toward these questions will be found of the greatest interest and stimulation, entirely irrespective of whether the reader agrees with his point of view in all respects. As may be judged from the chapter headings, the book examines more than the bases of physical science only, and will be found to contain, as the author says, "a singularly satisfying little philosophy".

The book makes charming reading; it is always entertaining and at times is touched with an immaginative insight truly poetical. It is good that physics has such a book. Pp. ix + 229, 8×5 inches. Yale University Press, New Haven, Conn., 1926. Price $3.00.

P. W. BRIDGMAN

Les Equations de la Dynamique de L'Ether. HENRI EYRAUD.—This monograph contains two chapters and an appendix. The first chapter develops the mathematical technique of the tensor analysis and discusses affine and metrical geometrics. In the second chapter the dynamics of the ether are developed from a minimum principle and the resulting equations are shown to contain Lorentz's electrodynamics as well as Einstein's theory of gravitation.—Pp. 66. Librairie Scientifique Albert Blanchard, Paris, 1926.

LEIGH PAGE

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY

MINUTES OF THE PHILADELPHIA MEETING

DECEMBER 28, 29, 30, 1926

The twenty-eighth Annual Meeting (the 142nd regular meeting) of the American Physical Society was held at the University of Pennsylvania, Philadelphia, Pennsylvania, on Tuesday, Wednesday, and Thursday, December 28, 29, and 30. The presiding officer was Professor Dayton C. Miller, President of the Society. The average attendance was about three hundred.

The annual joint session with Section B was held on Tuesday afternoon, with Professor William Duane, Chairman of Section B, presiding. The retiring Vice-President, Professor H. M. Randall, opened the joint meeting with an address entitled "Infra-Red Spectroscopy." This was followed by an address by Professor W. F. G. Swann on "The New Quantum Dynamics," and discussion of this topic by Dr. G. Breit and Professor J. H. Van Vleck. The attendance at this session was about four hundred.

On Wednesday evening, December 28, there was a dinner for the members of the Society and of Section B and their friends at the Hotel Bartram, attended by two hundred and four persons.

Annual Business Meeting.—The regular annual business meeting of the American Physical Society was held on Wednesday morning, December 29, 1926, at eleven o'clock. A canvass of the ballots for officers resulted in the elections for the year 1927 as follows:

For President;	K. T. Compton
For Vice-President;	Henry G. Gale
For Secretary;	Harold W. Webb
For Treasurer;	George B. Pegram
For Member of the Council, Three-year term;	Raymond T. Birge
For Members of the Council, Four-year term;	Paul D. Foote G. W. Stewart
For Members of the Board of Editors of the Physical Review, Three-year term;	G. Breit P. W. Bridgman L. W. McKeehan

The Secretary reported that during the year there had been 154 elections to membership. The deaths of 6 members had been reported during the year, 34 had resigned and 21 had been dropped. The total membership, including those newly elected, was 512 Fellows and 1341 Members, making a total of 1853.

The Treasurer presented his financial report for the year 1926. The Managing Editor presented the financial report for the Physical Review for the year 1926. In his report of the condition of the Review he stated that it had shown a loss for the past year, and was probably facing losses in future years. The financial reports were ordered printed and distributed to the members.

To enable the Society to provide adequate support for the Physical Review in future years, the Treasurer, on behalf of the Council, introduced the following resolution: *Resolved: That Article I, Section 1, of the By-laws be amended to read "The annual dues of fellows shall be fourteen dollars and of members ten dollars, payable on the 1st of January," this amendment to take effect January 1, 1928.* This resolution was passed by 44 affirmative votes to 7 negative.

Meeting of the Council.—At the Meeting of the Council held on December 28, 1926, three persons were elected to Fellowship, three were transferred from Membership to Fellowship, and twenty-nine were elected to Membership. *Elected to Fellowship:* F. W. Goucher, Karl F. Herzfeld, Fritz Zwicky. *Transferred from Membership to Fellowship:* Hugh L. Dryden, Carl H. Eckart, Francis D. Murnaghan. *Elected to Membership:* William H. Abbitt, Kenneth T. Bainbridge, Garnett F. Barnes, David G. Bourgin, Katherine Chamberlain, J. Davidson, Jr., Sophie W. Eldridge, C. W. Gartlein, Daniel E. Harnett, Marshall C. Harrington, Jos. E. Henderson, J. H. Hsu, Karl H. Hubbard, Carl Kenty, John J. Livingood, John B. Miles, Jr., L. W. Moench, P. M. Morse, Sister Mary S. Murray, Carl A. Pearson, R. J. M. Raven-Hart, C. M. Slack, Arthur P. Tanberg, W. Norris Tuttle, A. H. Wait, Harvey E. White, R. M. Williams, B. S. Woodmansee, W. Morris Young.

The regular program of the American Physical Society consisted of 77 papers, Numbers 1, 5, 11, 12, 17, 18, 19, 27, 43, 49, 50, 53, 66, 68, 70, and 73 being read by title. The abstracts of these papers are given in the following pages. An **Author Index** will be found at the end.

HAROLD W. WEBB,
Secretary.

ABSTRACTS

1. The absorption of beta-rays. J. A. GRAY and B. W. SARGENT, Queen's University.—An examination has been made of the absorption of the β-rays of radium E and uranium X in carbon, aluminum, copper, tin and lead. The former rays have the following approximate relative ranges (expressed in grams per cm^2), in these substances, viz., 62, 64, 71, 89 and 100. For the β-rays of uranium X, the corresponding numbers

are 78, 81, 82, 95 and 100. As the relative ratios of atomic weight to atomic number are 79, 82, 87, 94 and 100, the experiments indicate that the energy lost in an atom by the β-rays of uranium X is, on an average, proportional to the atomic number.

2. A new theory of the origin of the actinium series. T. R. WILKINS, University of Rochester.—It is suggested that the variation of tne radii of pleochroic haloes in rocks of various geological ages can be explained if the actinium series is considered as coming from an isotope of uranium I (actino-uranium I) whose decay-constant is several times that of uranium I. These parent isotopes are assumed to have been in radioactive equilibrium originally but in geological time actino-uranium has largely disappeared and today forms but several percent of uranium. From a study of haloes, conclusions are drawn regarding the decay-constants of actino-uranium and the time since equilibrium. On the basis of such a theory, a considerable fraction of uranium lead would be due to actinium and the ages of rocks calculated either from lead or helium content will be in error—probably as much as 40% in the case of the oldest rocks.

3. Possible dependence of frequency of characteristic x-radiation on the temperature of the target. J. H. PURKS and C. M. SLACK, Columbia University.—Recent papers by H. S. Read (Phys. Rev. April and Nov. 1926) indicate that the absorption of x-rays depends upon the temperature of the absorber. This result has been interpreted as possibly due to a shift of the K absorption limit through about 11 volts. At the suggestion of Prof. Bergen Davis we have investigated a possible change of frequency of Mo Kα with the temperature of the target. Water-cooled and standard Coolidge tubes were used. The energy was such as to make the target of the second tube white hot, the temperature being well over 1000°C, though it was not measured because of negative results. Narrow slits were used and narrow rocking curves obtained. Peaks could be located to 2 seconds of arc. The reflecting angle of calcite crystal for Mo Kα is about 24000 seconds, hence there is no change of 1 part in 12000 due to temperature. If the K limit is shifted as Read's results indicate, it may be due to a destruction of the outer levels of the atom without any appreciable change in the (K-L) difference.

4. Investigation of metal films by x-ray analysis. KARL HOROVITZ, International Research Fellow, University of Chicago.—Using the focussing x-ray vacuum spectrograph described some time ago ("Science," Sept., 1926), a method was developed of investigating metallic films deposited on glass and other surfaces in a high vacuum by any kind of atomic rays. The metallic films are then analyzed directly where they are originally formed without changing the vacuum or contaminating the metals with gases. Deposits of potassium have been investigated at liquid air temperature. Very thin, coloured or black layers did not yield a diffraction pattern. Potassium mirrors about 0.15 mm thick gave a diffraction pattern corresponding to a body centered cubic lattice $a=5.15$. Other metals and different methods of forming the deposits are now being studied.

5. The polarizing angle for x-rays. C. S. BARRETT and J. A. BEARDEN, University of Chicago (Introduced by H. G. Gale).—The classical theory of x-ray scattering predicts 90° for the polarizing angle of scattering from either an electron at rest or an electron moving with the final velocity of the quantum process. Intermediate velocities, as postulated in the quantum theories of Jauncey, Compton and Woo, give a polarizing angle of less than 90° and dependent upon wave-length. Dirac (Proc. Roy. Soc. **A112**, 405 (1926) predicts 90° on the basis of the new quantum dynamics. Previous experimental determinations of the angle have not been decisive. Using filtered radiation from a tungsten x-ray tube operated at 190,000 volts the polarization angle was measured by the ionization method. With wave-lengths of 0.215, 0.24, and 0.37A (as measured by absorption) the polorizing angle was found to be 90° 30′, 91° 20′ and 90° 50′ respect-

ively. Thus within the probable experimental error no shift from 90° or dependence on wave-length was observed. This is in agreement with the new quantum dynamics but notwith the theories of Jauncey or Compton-Woo, which predict 83° 53′ and 84° 10′ respectively as the polarizing angle for 0.215A.

6. X-ray coloration of kunzite and hiddenite. P. L. BAYLEY, University of Rochester.—Absorption curves have been obtained from 2000 to 300 mμ for a pink sample of kunzite and a yellow green sample of hiddenite both before and after exposure to x-rays. The kunzite had only one weak wide absorption band at 540 mμ. The hiddenite had bands at 1670, 1000, 630, 438, 432, 378, and 368 mμ. After x-ray treatment, the hiddenite showed only a slight increase in absorption below 440 mμ. However, the x-rays colored the kunzite very similarly to the hiddenite but slightly more bluish green (as has been noted by others). Bands which were not present before radiation occurred at 910 and 625 mμ. The positions of maximum transmission were 730 and 540 mμ which were nearly identical with those of hiddenite. No trace of the hiddenite bands below 500 mμ could be found in the radiated kunzite. The fact that by x-radiation there can be produced in kunzite absorption in the region 1250 to 450 mμ which is so similar to that of hiddenite, would suggest that the green color in both materials is due to a similar physical cause. The methods of production need not have been similar.

7. X-ray diffraction measurements on some of the pure compounds concerned in the study of Portland cement. E. A. HARRINGTON, Bureau of Standards.—Using the powder photographic method of x-ray analysis the crystal symmetry, lattice constants, and densities of Al_2O_3, Fe_2O_3, $Ca(OH)_2$, $3CaO \cdot Al_2O_3$, and $5CaO \cdot 3Al_2O_3$ have been determined. The values found for CaO, $CaCO_3$, and SiO_2 are added to complete the list of cubic, hexagonal, and rhombohedral crystals of important compounds in Portland cement research.

8. The crystal structure of magnesium di-zincide. JAMES B. FRIAUF, Carnegie Institute of Technology.—Crystals of the intermetallic compound, $MgZn_2$, were prepared and the crystal structure was determined from x-ray data furnished by Laue and rotation photographs. The crystal was found to have hexagonal axes with $a=5.15$A and $c=8.48$A. The unit cell contains four molecules. The effect of absorption in the crystal in determining the wave-length giving a maximum intensity of reflection in Laue photographs was used to confirm the dimensions of the unit cell. The atoms have the positions:
Zn: u, $\bar{u}$, 1/4; $2\bar{u}$, $\bar{u}$, 1/4; u, $2u$, 1/4; $\bar{u}$, u, 3/4; $2u$, u, 3/4; $\bar{u}$, $2\bar{u}$, 3/4; 0, 0, 0; 0, 0, 1/2
Mg: 1/3, 2/3, v; 1/3, 2/3, 1/2$-v$; 2/3, 1/3, 1/2$+v$; 2/3, 1/3, $\bar{v}$.
Where $u=0.830$ and $v=0.062$. The magnesium atoms have very nearly the arrangement that has been proposed by Bragg for the oxygen atoms in ice. The least distance between two magnesium atoms is 3.15A, between two zinc atoms, 2.52A, and between a magnesium and a zinc atom, 3.02A.

9. The relative probabilities of the photo-electric emission of electrons from Ag and Au. F. K. RICHTMYER and L. S. TAYLOR, Cornell University.—Data previously reported by one of us (F. K. R., Phys. Rev. January, 1926) indicated that the ratio, R_L^K, of the number of $K+L+M+\cdots$ photo-electrons to the number of $L+M+\cdots$ photo-electrons decreases from about 7.5 in the case of Mo to about 5.1 in the case of Pb. These data were approximate and were not in agreement with any of the existing theories. The theories of J. J. Thomson and of de Broglie require values of R_L^K large than above and increasing more rapidly with *decrease* in atomic number. The theory of Kramers requires values of R_L^K of about 5.1 and *independent* of atomic number. More careful data has now been taken through the K absorption limit of Ag and Au,

using narrow slits (about 5 x-units wide). The magnitude of the discontinuity in the mass absorption coefficients through the limit is determined with a precision of one percent. But the value of R_L^K computed from this discontinuity depends entirely on the magnitude of the correction for scattering. If a mass scattering coefficient, σ/ρ, of 0.8 be assumed for both Ag and Au, the value of R_L^K is 6.4—independent of atomic number as required by Kramers, but larger than predicted by him. If the Thomson (classical) value of σ/ρ be assumed (i. e., $\sigma/\rho=0.2$), then R_L^K for Ag is 6.0 and for Au is 4.4. Values of R_L^K cannot be determined unambiguously until better data on scattering coefficients is available.

10. A possible relation between radiation and ionization potentials of iron. OTTO STUHLMAN, University of North Carolina.—The critical potentials of iron, found in recent investigations by Thomas, Chu and Richardson and by Chalkline claim to possess the following term values in common, $M_{II\ III}$ at 54 volts, M_I at 93 volts and L_{III} at 706 volts. If we agree to retain the following (I) potentials, 11.1, 19. 4, 41.2, 54.6, 103.5, 169.4, as determined by Thomas and new (I) potentials of 5.72, 7.29, 11.14, and a (R) potential at 8.14 volts, then all critical (R) potentials published can probably be attributed to multiple impact.

11. The 29 volt critical potential of hydrogen. ROGERS D. RUSK, North Central College.—Low voltage arc characteristics for varying anode distances and gas pressures have been measured in hydrogen using a special tube containing two hot filaments and two nickel anodes. Striking and breaking potentials of one arc were observed when the region of that arc was illuminated by the glow from the other arc in the same tube at pressures below 0.2 mm. With increasing intensity of illumination the arc could be struck with great regularity at potentials down to the minimum maintaining potential for any given filament current, anode distance and gas pressure, but never lower. The lowest maintaining potential for the type of glow observed was 29 volts and it is suggested that this represents primarily a molecular excitation level capable of sustaining intense cumulative ionization and having a critical excitation period of the order of 10^{-8} sec. as indicated by the quenching effect of pressure change.

12. Spectral intensity distribution in a hydrogen discharge. E.W.TSCHUDI, Winthrop College, Rock Hill, S. C.—A cold-cathode discharge tube has an auxiliary tube attached from which cathode rays are projected against the main cathode. A photo-electric cell, attached to a monochromatic illuminator, is used to measure relative intensity distribution of H_γ and H_δ, respectively, from the main cathode through the cathode dark space into the negative glow with and without excitation of the auxiliary tube. When the main cathode is bombarded by the electron stream the intensity of spectral illumination in the negative glow is increased by about 20 percent. This increase does not result from the mere addition of an illumination which appears when the auxiliary tube is alone excited to the illumination of the main discharge, but may be attributed to the production of soft x-rays in the gas which are capable of exciting the gas molecules.

13. Excitation of spectra by atomic hydrogen. F.L. MOHLER, Bureau of Standards.—Hydrogen from a Wood discharge tube flowed into a tube containing metal vapor and the spectrum emitted by the mixture was photographed. Observations of Bonhoeffer (Zeits. f. Phys. Chem., **116**, 391 (1925)) with sodium and mercury are confirmed. Sodium and cadmium gave strong emission of their first resonance lines and no other lines or bands. Potassium showed the first resonance line faintly. Mercury gave the complete hydride band spectrum and also faint emission of the resonance line at 2537A. Caesium, magnesium, thallium and zinc gave no line or band spectra. The excitation energies of the observed lines and bands are, except for 2537 of mercury, less than 3.8 volts though

many lines of lower energy did not appear. There are two possible explanations of the radiation. The metal atom may be excited in a three body collision with two hydrogen atoms. In this case the entire energy of recombination of hydrogen, 4.38 volts, should be available for excitation. The second possibility is that first a hydride is formed and that this reacts with H to form H_2 and an excited metal atom. The available energy of excitation is the energy of recombination of H minus the energy of formation of the hydride. The second theory seems to offer the best explanation of the observations.

14. The absorption of ultra-violet light by organic vapors. ALPHEUS W. SMITH, CECIL E. BOORD AND C. S. PEASE, Ohio State University.—This paper gives a preliminary report of work being done on the absorption by organic vapors in the ultra-violet. An aluminum under-water spark served as a source of continuous radiation. The spectra were photographed by means of a Hilger E2 quartz spectrograph and the vapors were inserted between the source of light and the slit of the spectrograph in glass tubes with quartz ends. The intensities of tne absorption lines were determined by a Moll microphotometer. The following vapors have been studied,—benzene, diethyl ether, methyl normal amyl ether, and ethylene chlorohydrin. In each case the absorption spectrum consists of four or more prominent bands which are resolved into a number of lines of varying intensities. The photographic records from the micrphnotometer show that these bands are very similar in structure. Each band consists of a very prominent line with neighboring lines of less intensity lying on the side of the longer wave lengths. The observed lines are broad and also shaded toward the longer wave-lengths. They have the appearance of unresolved band spectra. The most prominent of these lines lie at approximately $\lambda = 2590$A, $\lambda = 2530$A, $\lambda = 2470$A and $\lambda = 2420$A. The intensity of the absorption changes with the composition and structure of the compounds. The other characteristics of the bands remain essentially unchanged.

15. New series in the spectrum of fluorescent iodine. F. W. LOOMIS, New York University.—Several new series are found in Wood's spectra of fluorescent iodine and their constants (d and γ) are measured. From these, $\bar{n}$, the vibrational quantum number of the fluorescent molecule before excitation, (taking $\bar{n}_0 = 0$ for simplicity) is calculated and in each case comes out nearly integral. Most of the series extend into the antistokes region as far as the order $p = -\bar{n}$. None of them extend further. Moreover the frequency of the origin of the band to which the resonance line of each series belongs, when calculated from d and the writer's values of the constants of the iodine absorption spectrum, agrees well, in every case, with the origin of a known band whose n'' is equal to the $\bar{n}$ previously calculated for the series. These results confirm the reality of the series and yield values of n' and n'' for each doublet in it. A plot of (n', n'') for all the fluorescent doublets which have been identified, suggests that the intensity diagram would show a pattern having maxima along roughly hyperbolic curves, analogous to that found by Birge for the β bands of nitrogen. Several of the fluorescent series have the same n' but very different m''s. Comparison of their intensities suggests that relative probabilities of transition do not appreciably depend on m'.

16. On the infra-red spectrum of mercury. VLADIMIR P. LUBOVICH, University of Colorado.—In the paper by McLennan and Shaver an account was given of a photographic investigation of the mercury spectrum from $\lambda = 6908$A to $\lambda = 11137$A. The spectrum was photographed in the first order of a diffraction grating, higher orders being cut off with Wratten filter No. 22. The present work seems to prove that due to a transparent filter and incorrectly measured wave-lengths, higher order lines were ascribed to the infra-red spectrum. The conclusion is reached partly through the analysis of McLennan and Shaver's work, partly by means of a new photographic study of the mercury spectrum with a prism instrument. The investigation also includes the measurement of wave-lengths up to $\lambda = 13670$A. Beyond this limit four more lines are detected, the last

one being in the neighborhood of λ27000A. Nineteen lines are identified photographically apparently for the first time. Among the newly photographed lines the line λ=10141A was suggested by McLennan and Shaver to be a doublet. The present work verifies the original observation of Paschen that it is a single line. In view of the contradictory results of previous investigations regarding the absorption of λ=10141A by non-luminous mercury vapor the author reexamines this question with a result which confirms the conclusion of McLennan and Shaver that no absorption exists.

17. Absorption spectra in the extreme ultra-violet. J. J. HOPFIELD, University of California.—Absorption spectra of nitrogen, air, acetylene, and carbon monoxide have been obtained with widely varying pressure. They show selective absorption and a region of continuous absorption on the short wave-length side. This region again shows selective absorption and abounds in maxima and minima when low enough pressures are used. Acetylene shows band absorption beginning at λ2300. At lower pressures maxima of absorption are found at λλ1520, 1480, 1430, and many other both narrow and wide bands to λ1000. Nitrogen shows besides the bands already found by Sponer strong continuous absorption beginning at λ990. Absorption occurs in the discharge tube also. The principal lines of the four ultra-violet series of N I are thus observed, and a group of lines λ1085 due to ionized nitrogen. A few carbon lines were found when CO was used. These are probably the resonance lines of this element. The Cameron bands of CO are found in absorption and prove directly that these arise from the normal state. 0–0 to 0–4 are observed. Four or five bands of an apparently new system in CO begin with either λ1696.9 or 1664.4 as the 0–0 band, and continue with λλ1634.0, 1604.9, and 1577.6 as consecutive members.

18. The ultra-violet band spectra of nitrogen. R. T. BIRGE AND J. J. HOPFIELD, University of California.—The ultra-violet nitrogen system previously analyzed by us (Nature **116**, 15 (1925)) has been greatly extended to include 60 bands between λ1250 and λ2025. More accurate measurements prove that the assignment of this system to NO is unjustified. Moreover, it has now been found by Sponer (Nature, in press) in absorption in cold nitrogen. It is the resonance system of nitrogen, corresponding directly to the fourth positive group of CO. The other weaker progression found by Sponer in nitrogen, as we have since proved, is absorbed *only* in the discharge tube, and is in fact merely the usual absorption spectrum of CO. We have identified two other progressions of emission bands lying between λ1030 and λ1520. Both have the same lower electronic level as the above nitrogen system, and extend this level to $n=18$. They locate two new electronic levels at 104,410 cm^{-1} and 103,660 cm^{-1}. The four electronic levels associated with the ultra-violet nitrogen systems are probably singlet levels, while the four levels associated with the familiar nitrogen systems are triplet. Transitions between the two types of levels are not in general to be expected, from theoretical considerations, and none have as yet been found in nitrogen.

19. Infra-red absorption by the N-H bond; in aniline and alkyl anilines. JOSEPH W. ELLIS, University of California, Southern Branch.—The infra-red absorption spectra of aniline, five monoalkyl anilines and five dialkyl anilines have been recorded below 2.8μ by means of a self-registering quartz spectrograph. Prominent bands of absorption, occurring at 1.47μ and 1.04μ for aniline, appear with diminished intensity for monoalkyl anilines and disappear for the dialkyl anilines. A band at 2.8μ exhibiting changes, analogously to these two, has already been announced by F. K. Bell (J. Amer. Chem. Soc., **47**, 2192, (1925)). The frequencies in mm^{-1} of these three bands are expressible by the parabolic formula, $\nu_n=375.8n-18.3n^2$, and are believed to constitute a non-harmonic series of vibrations characteristic of the N-H bond. The series is analogous to one already attributed by the author to vibrations of the C-H bond. Two other bands, apparently associated with the presence of the N-H bond, occur at 1.20μ and 2.00μ

for aniline. The former is not detectable in the spectra of monoalkyl anilines because of overlapping bands, but the latter is shifted to 2.05μ. A quantum theory explanation is offered as to the origin of these bands on the basis of combinations of N-H and C-H frequencies.

20. A new method of determining the time of appearance as well as the time of duration of spectrum lines in spark discharges. J. W. BEAMS, National Research Fellow, and ERNEST O. LAWRENCE, National Research Fellow, Yale University.—Light segments a few centimeters in length obtained by a method described elsewhere (see previous abstract) emanating during various time intervals after the beginning of a spark discharge fall upon a very sensitive photo-electric cell. Plotting the observed photo-electric currents against the time intervals elapsing between the beginning of the spark and the production of the light segments, there are obtained curves having significant changes in slope. Abrupt increases in the photo-electric current determine the time of appearance of the various spectrum lines while decreases in the current indicate their disappearance. The above method is very reliable and gives the time of appearance of the spectrum lines with a high degree of precision.

21. The arc spectrum of germanium. C. W. GARTLEIN, Cornell University (Introduced by R. C. Gibbs).—The wave-lengths of the lines in the arc spectrum of germanium have been measured in the region above 1860A with an accuracy of at least 0.1A. From these measurements the relative energy levels have been worked out and the jumps corresponding to 56 lines have been identified. In the normal state the atom contains two (p) valence electrons which give rise to the lower levels ^3P, ^1D, ^1S, with the ^3P lying deepest, as is predicted by the theory of Hund. The next higher levels arise from the electron configurations (ps) and (pd). The energy levels have been correlated with the ultimate and persistent lines found by other investigators. The arc spectrum of Ge closely resembles the arc spectra of Si, Sn, and Pb.

22. Stages in the excitation of the spectrum of indium. JOHN G. FRAYNE, Antioch College, and C. W. JARVIS, Ohio Wesleyan University.—The indium metal was vaporized at a temperature of 650°C in an iron cylindrical anode within a quartz tube. Electrons from an oxide-coated Pt filament passed through a cylindrical grid into a force free space where they collided with the atoms of indium vapor. The spectrum was viewed end on through a transparent quartz window. At 3.3 volts the lines $2p_1-2s$ and $2p_2-2s$ appeared. At 4.2 volts the additional lines $2p_1-3d$ and $2p_2-3d$ appeared. At seven volts higher members of the series appeared. At 13.2 volts the spectrum became very intense and lines appeared in addition to the recognized series lines. At this potential a second electron may have been detached from the atom, assuming that ionization occurred at seven volts. At 23 volts many lines appeared in the visible and near ultra-violet but most of them have been recognized as air lines. Using voltages as high as 80 no other lines appeared. The lines from the $2p_1$ level were consistently stronger than those from the $2p_2$ level at temperatures ranging from 600° to 800° C. The latter level is considered to be the lowest and should give the strong lines of the spectrum.

23. On the spectra of boron. R. A. SAWYER, University of Michigan, and F. R. SMITH, Pennsylvania State College.—Spectra of boron in the region λλ2300–5800 were obtained by the "vacuum spark" method, using electrodes of boron, and boron and carbon. The vacuum spark chamber was made of glass and so designed that considerable adjustment of the spark-gap could be made without opening the spark-box. The lines were photographed with a two-prism glass spectrograph and a Hilger 2E quartz spectrograph. After checking for impurities about ninety new lines were ascribed to boron. Starting with the term values of B I, B II and B III given by Millikan and Bowen, about twenty-five of these lines have been classified in series.

24. Energy level studies on metallic vapors using a high temperature tungsten furnace. O. S. DUFFENDACK and J. G. BLACK, University of Michigan.—Following in general the method originated by Duffendack in 1922, an electrically heated tungsten cylinder is clamped horizontally between heavy water-cooled leads and enclosed in a large water-cooled copper cylinder provided with observation windows and containing pure hydrogen. An insulated U-shaped tungsten or molybdenum trough extends axially through the furnace and holds the material to be studied. Absorption studies on copper vapor yielded new absorption lines at 2618.37, 2824.39, 2882.81, 2961.19, 3010.87, 3194.09 and 5782.08 all originating in the metastable $^2D_{2,3}$ level in agreement with Shenstone's analysis, together with previously reported absorption lines and copper-hydride bands. The copper lines 3247, 3274, 5106, 5700, 5782 and several copper-hydride bands were obtained in emission. These five lines originate in the $2^2P_{1,2}$ level. Experiments proved that this state was reached by absorption of resonance radiation rather than by thermal excitation. No absorption lines originated in this level. The metastable $^2D_{2,3}$ level from which absorption lines were observed is reached by thermal action. These experiments were made principally to test the furnace. It is being adapted for investigations of resonance radiations, critical potentials, and other properties of elements at high temperatures. It compares favorably with other furnaces and avoids difficulties due to oxidation and impurities.

25. On the Zeeman effect and the structure of the arc spectra of Cu and Rh. L. A. SOMMER, International Research Fellow, Harvard University (Introduced by E. A. Saunders).—Investigating the arc spectrum of Cu, Shenstone and the author are in agreement in the classification of the doublet term group ^2P, $^2\overline{D}$, ^2F which lies near the quartet term group ^4P, $^4\overline{D}$, ^4F, but reach different conclusions regarding the classification of the higher doublet term group ^2P, $^2,\overline{D}$ ^2F, and especially the term-groups *with negative term-values*. The author uses chiefly his own measurements of the Zeeman effect for the assignment of the terms, while Shenstone bases his designations mainly on line intensities. A more general formulation of the selection rule for k for jumps of one or more electrons is proposed. While the first (alkali-like) term-system (doublet-terms)corresponds to atomic states in wnich tne 4_1 electron rotates around the rest of the atom with its ten 3_2 electrons, the second system (doublet and quartet-terms) is due to states in which the outer electron rotates around an inner shell consisting of nine 3_2 and one 4_1 electron. One set of lines in the visible is associated with the simultaneous transition of two electrons. Of about 660 measured lines of the Cu-arc more than half are combinations within or between the two term-systems. From the series limits it is found that the removal of the 3_2 electron requires a potential 10.9 volts, while the 4_1 is bound with the well-known potential of 7.6 volts. In the Rh spectrum 50 percent of the lines measured in the arc are arranged in a definite term-system by means of the Zeeman effect data.

26. Absorption spectra of iron, cobalt and nickel. W. F. MEGGERS, Bureau of Standards, and F. M. WALTERS, JR., Carnegie Institute of Technology.—The under-water-spark absorption spectra, as well as the ordinary vapor absorptions, have been investigated by others, but not in sufficient detail in connection with the spectral structures for Fe, Co and Ni. Employing the apparatus and method described by Meggers and Laporte in the *Physical Review* for October, 1926, these spectra were reexamined throughout the visible and ultra-violet regions. Our spectrograms show 263 iron lines (2166 to 4404A), 340 cobalt lines (2137 to 4121A), and 225 nickel lines (2124 to 3858A) absorbed in the source. In each case, the majority of these are identical with the stronger lines of the arc-emission spectra, and practically all such lines are found to involve either the normal state or some low metastable state of the neutral atoms. The type of source used showed most of the metallic spark lines in emission but certain groups were present in absorption with low intensity. The latter involve the

lowest energy states of the ionized atoms. With the aid of these data on absorption the known spectral structures for neutral and for ionized Fe, Co and Ni have been confirmed, and many new levels have been established.

27. Spectra of the high-current vacuum arc. ARTHUR S. KING, Mount Wilson Observatory.—High-current arcs were used in a vacuum chamber at a pressure of about 5 mm of mercury, the arcs studied being those of iron, chromium, titanium magnesium, copper, and silicon, using electrodes of small diameter. The central vapor-stream of this arc, carrying 1500 amperes or more at 110 volts, is of intense brightness and shows a completeness of ionization usually obtainable only in high-potential sparks of very disruptive character. The spectrum is that of the ionized atom, lines of the second stage of ionization often appearing. The production of neutral-atom lines is evidently confined to the outer vapors of the vacuum arc, and only those arc lines which are little subject to broadening (usually low-temperature lines) retain sufficient density to register photographically. This arc is useful as a source of high excitation in a rarefied gas, operating without difficulty, and sufficiently bright to be photographed with high dispersion. The enhanced lines emitted, when of low energy-level in the ionized atom, usually show self-reversal, and in general the peculiarities of line-structure and the tendency to dissymmetry under high excitation are shown for enhanced lines in the same degree as the high-current arc in air shows these features for arc lines. These phenomena indicate the relative energy-levels and multiplet groupings of enhanced lines, also their degree of wave-length stability.

28. Some relations in the spectra of stripped atoms. R. C. GIBBS and H. E. WHITE, Cornell University.—Starting with the known values of the arc and spark spectra of one electron systems in all three of the long periods it has been found possible, by using the regular and irregular doublet laws as guides, to recognize the first pair of doublets in the principal series for stripped atoms as far as Mn_{VII} in the first long period, Zr_{IV} in the second long period, and Pr_{V} in the next period. The first pair of inverted diffuse doublets with satellite have also been located for Sc_{III}, Ti_{IV}, and V_{V}. These doublets possess very consistent frequency separations and the relative intensities of the lines are in agreement with the usual rule. Evidence is obtained indicating that in Sc_{III} we have the first instance, as originally predicted by Bohr, of a closer binding in a d orbit than in either a p or an s orbit. In fact, on the Moseley diagram the line for the $3d$ level crosses the lines for $4p$ and $4s$ levels in passing from K_{I} to Sc_{III}. The relative closeness of binding of the $3d$ orbit becomes even greater in the case of Ti_{IV} and V_{V}. The experimental data conforms very closely to both the regular and irregular doublet laws in the case of all first pairs of principal series doublets. Very consistent values for screening constants are obtained when the regular doublet law is applied to these doublets.

29. Two electron multiplets of the first and second long periods. H. E. WHITE and R. C. GIBBS, Cornell University.—Three characteristic multiplets arising from two valence electron systems of the first and second long periods of the periodic table have been found to follow very well the so-called regular and irregular doublet laws. These multiplets are of the type $^3D_{1,2,3}-{}^3P_{0,1,2}$, $^3D_{1,2,3}$, $^3D'_{1,2,3}$, and $^3D_{1,2,3}-{}^3F_{2,3,4}$, and have been extended in the first long period from Ca_{I} to Cr_{V}, and in the second long period from Sr_{I} to Cb_{IV}. The two electrons giving the above triplet levels are, in the initial state in $3d$ and $4p$ orbits while in the final state they occupy $3d$ and $4s$ orbits.

30. On metastable neon and argon. RICHARD RUDY, Research Laboratory, Nela Park.—The light from a Geissler tube (10 mm Hg, 100 mil-amp./cm²) was sent through the positive column of a second tube (15 cm long, .007 to .05 mil-amp. cm²). The absorption of 6402, one of the lines involving the metastable s_3 state, increased when the

pressure was lowered from 8 mm downwards and beyond the minimum discharge potential. This absorption had no influence upon the volt-ampere characteristic (<1/2 per cent), the metastable states being reestablished after emission (resonance). Strong absorption was also found in the negative glow. Increase of temperature at constant density increased the potential gradient for currents <1 milampere by shortening the so-called life of the metastable states in the same proportion as it reduces the absorption in neon or mercury. Argon added to neon did not seem to change the absorption as long as the discharge was chiefly maintained by neon. The next higher group of lines $s_5\ 3p_9$, $s_5\ 3p_8$ etc. in argon are not absorbed (<4 percent) under conditions where $s_5\ 2p_9$ shows 90 percent absorption.

31. Low pressure electric discharge in intense electric fields. C. DEL ROSARIO, Bartol Research Foundation and Yale University.—Attempts were made to pull electrons out of a cold fine filament by means of the intense electric field produced at its surface when it is made the inner member of a cylindrical condenser. Most of the experiments were done in high vacuum of the order of 10^{-8} mm Hg as measured with an ionization gauge. The fineness of the filaments used ($5\times10^{-4}-10\times10^{-4}$ cm diameter) made it possible to obtain intense fields with smaller potential differences than those used by previous investigators. Different sizes of filaments were tried in order to dissect out the influence of the field and that of the potential difference on the current. Using a platinum-sputtered quartz filament, the platinum coating was torn off before electrons could be pulled out. With platinum filaments the field could be raised to 2×10^6 volts/cm without producing a current greater than 10^{-11} amp. The potential current curves of former observers could however be closely duplicated by admitting a little air into the apparatus. This fact together with the absence of any noticeable effect of the size of the filament on this curve suggests that the currents obtained by previous investigators may have been due to low pressure gas discharge.

32. A pseudo photographic effect of slow electrons. JOS. E. HENDERSON, Yale University (Introduced by W. F. G. Swann).—While using a magnetic spectrograph it was found that photographic plates subjected to a beam of slow moving electrons showed a dark line at the position calculated from the constants of the apparatus. This line was present on the plate even before development. In a further investigation 500 volt electrons were allowed to fall on different materials including glass, quartz, calcite, platinum, copper, nickel, silver, aluminum, zinc, lead and brass. The discoloration appeared on all of these. This discoloration seemed to be characteristic of the material being bombarded both as regards appearance and chemical behavior. The marking on the glass had a very metallic lustre but was readily attacked by strong alkalies. The line on the platinum was unattacked by the alkalies but was removed readily by aqua regia. The discoloration disappeared from the glass when it was heated above 450°C in air. From the nature of the apparatus it does not seem probable that a deposit could in any way be coming from the cathode. The apparatus employed gave an electron beam of comparatively high intensity, the current in the beam being several micro-amperes. Exposures of a few hours were necessary in order to get a good discoloration.

33. Quantum theory of the specific heat of hydrogen chloride. ELMER HUTCHISSON, University of Pittsburgh.—The new quantum mechanics indicates that the specific heat of simple dipole molecules like those of HCl may be calculated using half integer rotational and vibrational quantum numbers in the expression for the energy and using $p_m=2m$ for the a priori probability (Cf. J. H. Van Vleck, Phys. Rev., Nov. 1926). Recently Hicks and Mitchell have computed the specific heat of HCl at various temperatures and its entropy using energy levels obtained from band spectra data but with

an a priori probability $p_m = 2m+1$. These values have been recomputed using the new quantum theory a priori probabilities. In this case it is found that the specific heat-temperature curve rises to a maximum above the classical value at about 12°K. There are not any experimental data at these low temperatures to confirm or contradict this maximum but at room temperatures the new specific heat curve agrees better with existing experimental values than that computed by Hicks and Mitchell.

34. A suggestion of an explanation of the long life of metastable atoms. G. BREIT, Carnegie Institution of Washington.—According to the recent theory of Schrödinger the term values of an atom are the characteristic values of E in his equation $[H, \psi] = E\psi$. The variable ψ when multiplied by its conjugate $\bar{\psi}$ gives the charge density. From this point of view the resultant electric moment of an atom due to the simultaneous presence of the states E_n, E_m is the element $q(nm)$ of the coordinate matrix q. The frequency of oscillation of the doublet is $\nu = 1/h(E_n - E_m)$. The above is Schrödinger's picture of radiation if $q(nm) = 0$. However, radiation may exist even in $q(nm) = 0$ corresponding to a coil aerial in radio for which the doublet also vanishes. Estimating the life of an atom on this basis, it is found to be of the order of almost a second. This is an agreement with the measurements [Dorgelo]. It is suggested, therefore, that the matrix mechanics represents only a first and rough approximation of the radiating properties of an atom and that Schrödinger's $\psi\bar{\psi}$ picture of electric charge density may be used to calculate radiation by means of classical formulas with retarded potentials even though matrix elements should vanish. A metastable atom is from this point of view analogous to a radio loop, while a non-metastable atom is analogous to an antenna.

35. Wave theory of the electron. W. P. ALLIS and H. MÜLLER, Massachusetts Institute of Technology.—The electron is considered as a wave of frequency $\nu = (mc^2 + eV)/h$ and wave number $\mu = c(m^2 - m_0^2)^{\frac{1}{2}}/h$ with which electricity is associated as energy is associated with an electromagnetic wave. Its group velocity $d\nu/d\mu$ is the velocity of the electron. The electricity is *always* "ether coupled." Uniform rectilinear motion or motion in certain orbits which are shorter than the wave-train are non-radiating. The quantum conditions are obtained as by de Broglie. The "quantum jump" is a continuous process in which charge gradually passes from the wave corresponding to the initial to that corresponding to the final state. During the process the waves form "groups" traveling with the velocity $\Delta\nu/\Delta\mu$ which obey the electromagnetic laws. In the Compton effect two plane waves form plane uniformly moving groups. The field must be zero on these groups. The scattered beam, superposed on the incident beam, is made to satisfy this condition and the conservation of energy and momentum relations result. In radiating hydrogenic atoms Δk groups move around the nucleus with the frequency $\Delta\nu/\Delta k$, and therefore radiate light of frequency $\Delta k \cdot \Delta\nu/\Delta k = \Delta W/h$. The indivisibility of the electron leads to the principle of selection.

36. The length of radiation quanta. ERNEST O. LAWRENCE, National Research Fellow, and J. W. BEAMS, National Research Fellow, Yale University.—Certain theoretical considerations of experimental facts lead to the conclusion that visible light quanta have lengths of the order of magnitude of 1 m. Closely allied to this conclusion, though quite independent of theory, is the length of time required for the photo-electric absorption of a light quantum by an electron, a time interval which has not been measured by experimental observation. By a refinement of a method previously described (J.O.S.A. & R.S.I., **13**, 597 (1926)) we have succeeded in producing flashes of light of the order of magnitude of 10^{-10} sec. duration, i. e., pulses of radiation a few centimeters in length. The average intensity of these flashes was roughly from a hundred to a thousand times greater than that of a 10 ampere arc. This fact in conjunction with a photo-electric cell of great sensitivity has enabled us to measure the photo-electric effects produced by these short pulses of light. Our results show that the magnitude

of the photo-electric effect per unit incident energy is independent of the length of the light pulses, and therefore, that light quanta are less than 3 cms in length and electrons absorb radiation quanta photo-electrically in less than 10^{-10} sec.

37. Effect of a magnetic field on the dielectric constant. J. J. WEIGLE, University of Pittsburgh.—Assuming a molecule or atom possessing magnetic and electric moments perpendicular to each other the effect of a magnetic field on the dielectric constant has been calculated by the methods of the classical statistical dynamics. It is assumed that at high temperatures the classical theory leads to the same results as the new quantum dynamics. For the average electric moment in the direction of the electric field (perpendicular to the magnetic field) the expression obtained in the first approximation is $\mu^2E/3kT$ where μ is the electric moment, E the electric field intensity, k the Boltzmann's constant and T the absolute temperature. This expression is the same as that obtained if there were no magnetic field present and might explain the negative experimental results of L. Mott Smith and C. R. Daily (Phys. Rev. Nov., 1926). Thus it does not seem necessary to reject Langevin's theory of Paramagnetism as has been suggested (Huber Phys. Zeit. **27**, 619 (1926)).

38. The quantization of the rotational energy of the polyatomic molecule by the new wave mechanics. ENOS E. WITMER, National Research Fellow, Harvard University.—For the purpose of quantizing the rotational energy the polyatomic molecule may be regarded as a rigid body with three principal moments of inertia, A_x, A_y, A_z. Assuming A_z to be the greatest or the least of these three quantities, let $a=\frac{1}{2}(1/A_x-1/A_y)$, and $c=1/A_z-\frac{1}{2}(1/A_x+1/A_y)$. Then $a/c\leqq 1$. The new wave mechanics gives the following formula for the energy, E, as a function of the quantum numbers:

$$E=(h^2/8\pi^2)\{m(m+1)\tfrac{1}{2}(1/A_x+1/A_y)+n^2c+\textstyle\sum_{r=1}^{\infty} f_r(m,n)a^{2r}/(c^{2r}-1)\},$$

where $f_1=\frac{1}{4}[m^2(m+1)^2/(n^2-1)+2m(m+1)-3n^2]$.
The quantum numbers m and n are integers, and $n\leqq m$. The process of solution apparently enables one to determine as many of thecoefficients f_r as are desired. This formula is very similar to the one given by the classical quantum theory (cf. Witmer, Proc. Nat. Acad. Sci. October, 1926). The convergence of this series for values of a/c in the neighborhood of unity remains to be considered.

39. The significance and scope of the idea of frequency in physics. WM. S. FRANKLIN, Mass. Inst. of Technology.—Exponential (or periodic) solutions of the wave equation are essentially necessary when a bounded system is being considered; such solutions for extended media are merely simple and convenient. Periodic solutions for extended media are physically justifiable because wave disturbances generally originate in quasi-closed systems, and such solutions for extended media are useful because they are easily formulated mathematically and because the phenomena of dispersion, of interference and of diffraction are steady for periodic waves. The advent of the Bohr relation $W=h\nu$ raised the idea of frequency to an exalted position which was extremely puzzling from the physical point of view, and the Bohr relation accentuated the non-critical use of the idea of frequency which was widely prevalent before Bohr's theory came forth. The Schrödinger wave mechanics brings us sharply back to the recognition of frequency as an ideal, because Schrödinger's mechanics is based on a generalized wave equation of which the only mathematically feasible solutions are exponential solutions and because Schrödinger attempts to formulate only those solutions which originate in closed or quasi-closed systems.

40. Influence of temperature on selenium photo-sensitivity. ROBERT J. PIERSOL, Westinghouse E. & M. Co., E. Pittsburgh.—Previous results on the influence of temperature on selenium have covered a range above 0°C. Various investigators have interpreted these data as either due to metallic conduction or due to electrolytic con-

duction. Experiment has shown that the dark current of a certain selenium cell decreases from 1×10^{-3} amperes at room temperature to less than 5×10^{-10} amperes at liquid air temperature, while the light current (due to one hundred foot candles intensity) decreases from 6×10^{-3} amperes to about 5×10^{-3} amperes with the decrease in temperature. This points to the fact that the dark current is entirely due to thermal conduction. Since H. E. Ives has shown that on cooling potassium from room temperature to liquid air temperature, due to increase in work function, the photo-electric current is decreased about 25 percent; it would appear that the light current in selenium is due to photo-electric conduction. As noted, a selenium cell at liquid air temperature gives a ratio of 1×10^{7} between the current due to 100 foot-candles and the dark current, thereby forming the most sensitive photometric instrument known for the measurement of feeble light intensities.

41. Actino-electric effects in argentite. W. A. SCHNEIDER, Washington Square College, New York University.—Actino-electric effects are observed in argentite and it is shown that the seat of conversion of light into electronic energy occurs both at the contacts as well as at certain spots on the crystal. The effect is found to be absent if the crystal structure is destroyed. The actino-electric current-intensity curves show a peculiar secondary effect at certain intensities, varying for different samples, however. On investigation of the actino-electric e.m.f.'s with reference to varying times of exposure and constant times of recovery it is found that an exponential relation exists between them which can be represented by $i=ae^{-bt}$. The "b" however is not a constant but increases with time of recovery and is the determining factor in the dark current and photo-electric hysteresis of the crystal. It may be very intimately connected with the positive part of the primary photo-electric current as described by Gudden and Pohl.

42. Photo-electric emission as a function of composition in sodium-potassium alloys. HERBERT E. IVES and G. R. STILWELL, Bell Telephone Laboratories, Inc.—The entire series of alloys of sodium and potassium have been investigated with respect to the relative values of the photo-electric currents produced by light polarized with the electric vector in and at right angles to the plane of incidence. The pure metals when molten exhibit values below three for the ratio of the two emissions; the alloys show *three maxima* at compositions approximately 20, 50 and 90 atomic per cent of sodium, with values from 10 to 30 for the ratio; the minima between show low values approximating those for the pure metals. The maxima and minima of the ratio of emissions are due to complicated variations in magnitude of the two emissions compared.

43. Some properties of Geiger counters. R. D. BENNETT, National Research Fellow, Princeton University. (introduced by H. D. Smyth.).—In the course of an investigation of the properties of Geiger counters they were found to be sensitive under certain conditions to ultra-violet light. The points used were of the sphere type and of platinum. Apparently the action comes about by the release of a photo-electron from the surface of the sphere-point. The maximum effective wave-length was about 2725A, corresponding to a work function of 4.54 volts, nearly that for platinum. Measurement of the photo-electric effect from a platinum surface in air at atmospheric pressure indicated that the number of pulses recorded was of the same order of magnitude as the number of photo-electrons released. A measurement of intensities across interference fringes in the ultra-violet gave variations similar to those recorded by other methods. Photo-electrons from the wall of the chamber, positive ions or electrons from a filament at about 300°, or ions blown in with gas, have proved sufficient to excite this type of counter. The number of pulses recorded depends markedly on the applied potential and may vary fivefold within the active range of any particular counter. Counters of this type have been made having less than one "stray" per half hour.

44. The life history of an adsorbed atom of caesium. J. A. BECKER, Bell Telephone Laboratories, Inc.—Previous work (Phys. Rev., August, 1926) indicated that when a caesium atom strikes a hot tungsten surface it may retain its valence electron, share it with the tungsten, or lose it completely. The adsorbed ions produce enormous changes in the thermionic and evaporation characteristics. A further analysis shows that the average life of an absorbed atom under equilibrium conditions is N/A, where N is the number of absorbed atoms and A the arrival rate. Both can be determined experimentally. When the filament is at 660°K and the arrival rate that corresponding to caesium at 20°C, the surface is completely covered and an atom stays on it for one second. For a temperature of 620°K, smaller arrival rate and complete covering the life is about one minute. At times "edges" separate the filament into two regions covered to about 1 percent and 15 percent. Several different experiments show that this edge must be about .03 centimeter wide. For part of this edge more caesium evaporates than arrives, and conversely. Hence atoms must move from one part of the edge to the other. Consequently the atoms must cover distances a million times their diameter.

45. Interpretation of data dealing with thermionic emission. W. R. HAM, Pennsylvania State College.—Equations for thermionic emission are of the form $i=AT^n\epsilon^{-b/t}$ the most commonly used values of n being $\frac{1}{2}$ or 2. The validity of this equation is determined by substituting values of i and T in the equation $\log i-n \log T+b/T=\log A$, and ascertaining whether a straight line is obtained when values of $\log i-n \log T$ are plotted against $1/T$. It is shown mathematically that a straight line may be obtained for all values of n from $-\infty$ to $+\infty$ including $n=0$ provided b is a suitable function of b_0 and T and therefore no improvement in accuracy of values of i and T or increase in their range can differentiate between various values of n. Hence to obtain a value of n experimentally, independent knowledge concerning A or b must be obtained. Using the value of b obtained calorimetrically by Davisson and Germer, together with their data for thermionic emission for tungsten, the equation $i=A\epsilon^{-b/T}$ is found to fit with great exactness. Values of b and A for certain other elements are computed on this basis. From a quantum standpoint according to Wien, a value $n=0$ demands that the concentration in metals of electrons available for thermionic emission at a particular T be relatively small.

46. Technique of the Dufour cathode ray oscillograph for the study of short time occurrences. G. F. HARRINGTON and A. M. OPSAHL, Westinghouse E. & M. Co., E. Pittsburgh (Introduced by C. E. Skinner).—In general, methods, circuits and procedure are set forth for using the Dufour plate-in-vacuum cathode ray oscillograph for studies of phenomena of such short time duration as to preclude the effective use of any other known oscillograph. Phenomena where such a method of analysis can be used to advantage are: dielectric breakdown in general, dielectric spark lag, characteristics of gaseous conduction, and behavior of electrical systems when subjected to surges. It is found that the time for the cathode beam to complete its path is so short that mechanical synchronizing devices are considered relatively unsatisfactory. Circuits are given for use in exciting the oscillograph, then initiating the transient condition to be recorded. It is also made possible to have voltage surges from the circuit being studied switch on the oscillograph and record themselves. The arrangement of apparatus is shown together with sufficient information so that it may be duplicated readily. Conditions and precautions are given for recording the coordinates that can be obtained conveniently with one cathode stream. These relations are: phase relations, voltage-time, current-time, voltage-current, voltage-current-time. The cathode ray oscillograph records these relationships accurately if proper care is taken with the circuits and checks and made to make certain that effects due only to the measuring circuits are eliminated.

47. A hot wire vacuum gauge. A. L. HUGHES and A. M. SKELLETT, Washington University, St. Louis.—A gauge was needed for following fairly rapid changes of pressure between .1 mm and .00001 mm. A 1-mil tungsten filament, 5 cms long, was mounted along the axis of a glass tube connected to the vacuum system. A current from a 4-volt storage battery was passed through the tungsten filament in series with an approximately equal and adjustable resistance R. With the highest attainable vacuum, the potential drop along the tungsten wire in the gauge was balanced against a 2-volt storage battery, using a galvanometer as an indicator, and varying R slightly to secure an exact balance. Using hydrogen to calibrate the gauge, it was found that the deviations from a balance were accurately proportional to the pressure over a range from .000007 mm to .28 mm. The lower limit can no doubt be decreased still further by taking special precautions to maintain constant conditions.

48. A new selective radiometer of molybdenite. W. W. COBLENTZ and C. W. HUGHES, Bureau of Standards.—Previous communications described samples of molybdenite having closely adjacent spots which generate positive and negative actino-electric current. Although practically no electric current is obtained on exposing the whole crystal to light either spot can be used as a radiometer. Recently discovered samples exhibit only one polarity, producing a large galvanometer deflection when the whole crystal is exposed to radiation of wave-lengths shorter than 1μ. In the darkened laboratory, connected with a d'Arsonval galvanometer, under a daylight illumination of 0.8 foot-candle the molybdenite crystal developed an e.m.f. equivalent to 1 f.c. = 3×10^{-4} volt. Connected with a high-resistance d'Arsonval galvanometer, deflections of 1.5 mm were observed in moonlight of only 0.008 f.c. Connecting the samples of molybdenite with a millivoltmeter, on exposure to the sun, under a normal illumination of 8,000 foot-candles, the deflection was 3 to 4×10^{-4} volt or 1 f.c. $=4\times10^{-8}$ volt; i. e., increasing the illumination intensity 8,000-fold decreased the intrinsic sensitivity about 130-fold. In spite of this lack of proportionality for high intensities (preventable perhaps by exposing only the most sensitive spot) this device has applications as a selective radiometer, rivaling the gas-ionic photo-electric cell in quickness of action and requiring no external battery.

49. The absorption of radio waves in the upper atmosphere. E. O. HULBURT, Naval Research Laboratory, Washington, D. C.—The absorption of radio waves in the upper atmosphere, put to one side in the theory of Taylor and Hulburt because of its smallness, has been calculated on the assumption that it results from collisions between the electrons and molecules of the atmosphere. Formulas are derived for the dispersion and absorption of the variously polarized waves, and quantitative agreement is indicated with observed data of ranges and degredation of intensity with distance from the transmitter. It is pointed out that as these data become more extensive they may lead to more exact knowledge of the electronic and molecular pressures overhead.

50. Propagation of electromagnetic waves along co-axial cylindrical conductors separated by two dielectrics. N. H. FRANK, Massachusetts Institute of Technology.—A solution of the Maxwell equations for a harmonic electromagnetic wave propagating along co-axial cylindrical conductors separated by two dielectric media has been obtained. The velocity of phase propagation of this wave is given by

$$v^2=(c^2/\epsilon_1\epsilon_2)\ (\epsilon_1\ln\ (r_3/r_2)+\epsilon_2\ln\ (r_2/r_1))\div(\ln(r_3/r_2)+\ln(r_3/r_1))$$

if the conductors and dielectrics are considered perfect. c is the velocity of light in vacuum, r_1, r_2, r_3 the distances from the center of the cable to the outsides of the inner conductor, first dielectric, and second dielectric respectively. ϵ_1 and ϵ_2 are the dielectric constants of the first and second dielectrics respectively. An experimental investigation of this formula by an extension of a method employing the Lichtenberg figures (Phys.

Rev. **25**, 865, (1925)) using ethyl alcohol, rubber and air as dielectrics and copper conductors showed that the above formula was satisfied within an experimental error of about 2 percent. Although the Lichtenberg figures are obtained by the use of an aperiodic pulse, the application of the above relation to this case can easily be justified, since the velocity given by the formula is also the velocity of propagation of the wave front even when the dielectrics and conductors are not perfect.

51. Subfundamental piezo-electric vibrations in quartz plates. J. R. HARRISON, Wesleyan University.—With a new type of piezo-electric crystal mounting, it has been found possible to obtain piezo-electric reactions of very much lower frequency than that of the transverse fundamental, first described by Cady (Proc. I. R. E. **10**, 83 (1922)). The "transverse fundamental" is the frequency of the compressional wave in the direction of the largest dimension of the plate, both ends being free. The new mode of vibration is also different from any previously observed in that it is dependent to a large degree on more than one crystal dimension. The crystal mounting is so designed that the electric field is applied to two areas which are symmetrically disposed with respect to the longitudal axis of the quartz plate, and the polarities in the quartz are in opposite directions. With the electric field applied in this manner, piezo-electric crystals operate successfully either as resonators or as oscillators at this subfundamental frequency. The luminous glow emitted by crystals when resonating in a low pressure chamber, lately described by Giebe and Scheibe (Elektrotech. Zeit. **13**, 380), can also be observed at the subfundamental frequency, the luminosity presenting striking peculiarities which still await explanation.

52. Factors affecting the constancy of quartz piezo-electric oscillators. EARLE M. TERRY, University of Wisconsin.—A study has been made of the effect of mechanical stresses, temperature, and circuit constants upon the frequency of an oscillating plate of quartz connected in the usual way across the grid-filament elements of an electron tube, a tuned resonance circuit being placed in series with the plate. Frequency changes were measured by determining the change in pitch of the audio frequency beat note between this oscillator and a similar one furnishing a constant frequency. Various kinds of deformations were produced by resting the plate on a three point support and applying forces at a single point on its upper surface at different positions. For loads up to 500 grams the frequency change is of the order of one part in 500,000 per gram, the change being sometimes positive and sometimes negative, depending upon the type of deformation. The crystal was later placed in an enclosed chamber and subjected to air pressures of 20 atmospheres. The frequency decreased by approximately one part in 74,000 per atmosphere, the rate of change increasing somewhat with the pressure. A theoretical study has been made of four commonly used circuits in which the crystal is replaced by its electrical equivalent, as given by Cady, and an expression for the resultant frequency obtained, holding within the limits of experimental error.

53. Precise determination of frequency by means of piezoelectric oscillators. J. TYKOCINSKI-TYKOCINER, University of Illinois.—The oscillating current whose frequency is to be determined is inductively superimposed upon the oscillations of a piezoelectric oscillator. The plate current of the driving thermionic oscillating tube is compensated by a potentiometer arrangement so that the current variations can be observed by a microammeter. The relation between the plate current of the piezoelectric oscillator and the exciting frequency was investigated experimentally. The curves show a sharp current maximum and minimum with an intermediate steep line crossing the zero current abscissa. The point of intersection corresponds to resonance. If the exciting frequency equals exactly the fundamental frequency or a harmonic of the piezoelectric oscillator, no influence whatsoever is exerted upon the plate current. But a deviation

of 1.15 of the frequency measured (294100 per second) can still be detected when the quartz crystal is clamped between two electrodes. With the crystal free, frequency variations less than one in a million are detected by a violent vibration of the microammeter pointer. The plate current variation in the measured circuit is of a different character and less pronounced.

54. High pressure powder contact rectifier. J. E. LILIENFELD and C. H. THOMAS, Davy Electrical Corp.—This rectifier makes use of the known contact combination, aluminum to cupric sulphide. It has been realized that the pressure is of importance with respect to the rectification, and therefore with a certain available compressing force, a definite contact area has to be maintained. It appeared later that highly compressed CuS powder offers just enough flexibility at its surface to secure intimate contact with the metal provided sufficient pressure is being maintained. The rectifier consists of cells made from a limited area about 25 square mm against a thin layer of CuS which has been forced into non-polarizing nickel cups. A compression force of about one thousand pounds is supplied by an *helical* spring. The resistance of the cell decreases until a critical pressure is reached. Every rectifier of the present size will deliver 2.5 to 3 amperes d.c. at 2 volts and on a lower amperage, higher voltage up to 3½ volts. A difference of the characteristics is noticeable between a pure resistance and an inductance load. Oscillograms of the current through a resistance load show complete and distortionless full wave rectification, while those of the current through a new filter circuit of inductances and resistances show suppression of the ripple to less than one percent of the total voltage.

55. A correlation between the power loss, dielectric constant and conductivity of various glasses. LOUISE S. MCDOWELL and HILDA BEGEMAN, Wellesley College.—Values of power factor, dielectric constant and resistivity are given for six glasses of widely varying resistivity. In general the order of decreasing conductivity is found to be also the order of decreasing power factor and decreasing dielectric constant. Exceptions to this order are noted and an explanation of the correlation based on electron theory is proposed.

56. Mechanical forces between electric currents and saturated magnetic fields. VLADIMIR KARAPETOFF.—The general case considered is that of N independent electric circuits placed in a medium of variable permeability and subject to saturation, in parts or as a whole. The problem is to determine the component (in a given direction) of the mechanical force acting upon one of the electric circuits, upon a group of circuits, or upon a group of circuits with part of the magnetic medium rigidly attached to them. Use is made of the expression for the stored electromagnetic energy, W, of the system, assuming all the electric circuits to be first open and then closed one by one. Such a treatment necessitates a number of partial saturation curves, giving the linkages with the individual electric circuits when some of the other circuits are closed and the rest are open. A virtual displacement, δs, is then given to the part of the system under consideration, keeping the linkages or the currents constant, and the force, F, is determined from a comparison of the work done, $F \cdot \delta s$, and the change in the stored energy, δW. It is shown that the familiar reciprocal relationship for the mutual inductance, $M_{21} = M_{12}$, in a medium without saturation, can be generalized to a more involved integral expression for a saturated medium.

57. Thermal agitation of electricity in conductors. J. B. JOHNSON, Bell Telephone Laboratories, Inc.—Ordinary electric conductors are sources of random voltage fluctuations, as the result of thermal agitation of the electric charges in the conductor. The average effect of the fluctuations has been measured by means of a vacuum tube amplifier, where it manifests itself as a component of the phenomenon commonly called

"tube noise." A part of the "tube noise" arises in the first tube and other elements of the apparatus; the remainder in the input resistance, with a mean square voltage fluctuation $(V^2)_m$ which is proportional to the resistance R of that conductor. The ratio $(V^2)_m/R$, of the order of 10^{-18} watt at room temperature, is independent of the material and shape of the conductor, but is proportional to its absolute temperature. In the range of audio frequencies, at least, the noise contains all frequencies at equal amplitudes. The noise of an input resistance of only 5000 ohms may exceed that of the rest of the circuit, so that the limit of useful amplification is at times set by the thermal agitation of charges in the input resistance of the amplifier.

58. The electrical resistance of metals as a function of pressure. A. T. WATERMAN, Yale University.—Assuming that the effect of hydrostatic pressure on the electrical resistance of metals is solely due to the accompanying volume change, the author's expression for the electrical resistance $R=CT^a e^{b/T}$ has been shown (Phys. Rev. 25, 4, p. 585) to be in agreement with experimental data on the pressure effect, provided the rate of change of b with volume is constant. Theoretical development of the influence of pressure on resistance, involving the effect of pressure on the chemical equilibrium postulated between atoms, ions and electrons within the metal, indicates that the pressure coefficient of resistance $1/R\,dR/dp$ is given by $\frac{1}{2}C+(1/2RT)(d^x/dp+\delta v)$, where $C=$ compressibility, $x=$energy change involved in the assumed reaction liberating electrons within the metal, and $\delta v=$a possible volume change accompanying the reaction. x may be expressed as the difference between the mean potential energies of an electron in the bound and in the free states. On calculating the compressibility (assuming only electrostatic forces) in terms of these quantities it appears that the change in resistance with pressure is chiefly due to a change in the mean potential energy of the free electrons. Furthermore, for elements in the same column of the periodic table, the rate of change with volume of the mean potential energies of both the bound and the free electrons is in approximate linear relation to the atomic number.

59. Molecular fields. DAVID G. BOURGIN, Lehigh University.—The treatments of statistical problems arising in physics which are based on direct extension of formulae, which are rigorously true for small values of n, have usually proved extremely complicated and have been discarded in favor of the methods of statistical mechanics. The recent statistical researches of Pearson provide a basis for development of a direct method which does not suffer from the objection of awkwardness. The advantages of this direct method are the greater transparency of the calculations and the fact that the number of necessary approximations may often be cut down or made more plausible. In the particular problem of molecular force fields, assuming random angular distribution under no impressed forces, an expression has been derived for the probability that the resultant field lies between F and $F+dF$. This fundamental expression has been evaluated for the case of a gas using current approximations. Some of the overlapping results of Holtsmark and Gans for this case are confirmed.

60. A general theory of the electrical properties of surfaces of contact. RICHARD D. KLEEMAN, Union College.—In a previous paper (Phys. Rev. **20**, 174–185 (1922)) the writer developed a theory of the e.m.f. associated with the part of a solution in contact with a metal plate. This theory is now extended to include the plate itself, and further generalized to apply to any two substances or mixtures in contact in any given state. The e.m.f. between two given points, one of which is situated in each substance, is expressed in terms of the coefficients of diffusion and the mobilities of the ions and molecules under the action of forces due to an asymmetrical distribution of matter and electricity, and externally applied electric fields. It is usually impossible to predict how these quantities vary from one part to another. But from the general nature of the

equations obtained the existence of a number of effects some of them still unknown can be predicted. A systematic experimental study of these effects is being undertaken.

61. Theory of cell with liquid junction. PAUL B. TAYLOR, University of Pennsylvania.—A simple integral is derived for the e.m.f. of the general cell with liquid junction in terms of transference numbers and molecular free energies. The transference numbers are made to depend upon the solution of a set of differential equations for the interdiffusion of two electrolytes each consisting of any possible mixture of ions. These equations involve the ionic mobilities and the molecular free energies, but not the free energies of the individual ions. It follows that the e.m.f. of a cell with liquid junction is not a function of ionic free energies and so can not possibly be manipulated to yield these quantities. Thus the values found in the literature purporting to measure hydrogen ion free energy, the so called Ph numbers, when based on such cells are quite unjustified. Henderson has given a formula, recently improved by Harned, for the p.d. of the liquid junction. This p.d. can not be found in terms of thermodynamic data (except at infinite dilution), but the formula modified to yield cell e.m.f. is a useful first approximation to a solution of the differential equations. A solution which may be considered a second order approximation has been derived.

62. The absolute zero of the externally controllable entropy and internal energy of a substance or mixture. R. D. KLEEMAN, Union College.—The internal energy of a substance or mixture may be divided into two parts, one of which is externally controllable, and therefore a function of temperature and volume, while the other part is not. The entropy may similarly be divided into two parts. It is shown that in thermodynamics we are only concerned with the controllable internal energy and entropy and that these quantities may have zero values. The temperature and volume corresponding to these zero values may be obtained by means of the theorem that the specific heat of a mixture kept at constant volume can only have positive values, which may be said to follow from our conceptions of temperature and heat content, and the postulate that the increase in pressure per unit increase in temperature at constant volume cannot be infinite, which will probably be readily admitted. It is then obtained that the controllable internal energy and entropy of a substance or mixture in the condensed state in contact with its vapour at the absolute zero of temperature have zero values. Formulae for the controllable internal energy, entropy, free energy and potential corresponding to any density and temperature may then readily be deduced.

63. On the dependence of ionic mobility on the nature of the medium. HENRY A. ERIKSON, University of Minnesota.—If air ions pass through air containing impurities such as carbon dioxide or water vapor, it is found that the mobility diminishes as more of the impurity is added. The conditions involved are such as to lead to the conclusion that the change is due to the change in the medium and not to a change in the ions.

64. Variation with state of the optical constants of caesium. J. B. NATHANSON, Carnegie Institute of Technology.—The optical constants of caesium were determined for the solid and liquid states, for wave lengths 5400, 5890, and 6410 A. Observations were made at 23°C and 33°C, the melting point of caesium being 26°C. The glass cell containing the caesium mirror was warmed by means of a small electrical oven enclosing the mirror and containing suitable apertures for the incident and reflected light rays. The method of observation was that previously employed. (Phys. Rev. **25**, 75 (1925).) The optical constants were computed by means of Drude's equations. When the metal changed from the solid to the liquid state, it was found that the angle of azimuth of restored plane polarization, as well as the phase difference between the components of the light vector parallel and perpendicular to the plane of incidence, changed very little, thus producing only slight changes in the values of the coefficient of absorption, k, the

index of refraction n, and the reflecting power R. For example, for λ5400A and solid caesium, $k=3.74$, $n=0.308$, and $R=0.595$, while for liquid caesium, the corresponding values are 3.66, 0.310, and 0.588.

65. An unusual magnetostrictive effect in Monel metal. S. R. WILLIAMS, Amherst College.—Magnetically, nickel is a most interesting metal. No less so are its alloys as permalloy, for instance, demonstrates. Monel metal, an alloy of nickel and copper, has also some very interesting magnetic properties. Among these is the fact that it loses its magnetic properties in the neighborhood of 100°C. The Joule magnetostrictive effect was studied in both hot and cold rolled rods of Monel metal. Some behaved like cobalt and others like nickel. The most interesting effect was, that if a magnetizing field of about 1000 gauss was left impressed on the Monel metal rod, it would continue to shorten, although the field was not varied, until the heat from the coil finally penetrated and the two effects worked against each other. This after effect in Monel metal is four to five times greater than the change in length due to varying the imposed magnetic field, whereas the after effect in nickel is only about 1/20 of the main Joule effect. The biggest magnetostrictive effect in Monel metal is that due to time whne a certain field is applied and maintained constant.

66. Magnetic susceptibility of single-crystal elements. C. NUSBAUM, Case School of Applied Science.—A modified form of the Terry torsion balance is being used for the determination of the magnetic susceptibility of a number of single-crystal metals along their respective crystallographic axes. The sample is mounted on a specially designed table and may be rotated in the magnetic field around any given axis. An investigation has been made on tellurium which has a three-fold axis of rotational symmetry. Curves show the variation of the susceptibility with the angle of rotation as the crystal is rotated around any of its axes. A similar study is also being made of the single crystals of Cd, Bi, Sb, Sn, and Zn.

67. The effect of wave-length on the differences in the lags of the Faraday effect behind the magnetic field for various liquids. FRED ALLISON, Alabama Polytechnic Institute.—Through the employment of a method by means of which two magnetic fields can be applied and removed simultaneously, it has recently been found by Beams and Allison that in various liquids there is a lag of the Faraday effect behind the magnetic field. This lag varies with different liquids and the differences in these lags for several liquids were determined with a precision of 0.4×10^{-9} sec. The present paper extends the work to an investigation of the differences in the lags of the Faraday effect for several liquids when different wave-lengths of light are used. The liquids studied were carbon bisulphide, carbon tetrachloride, chloroform, benzene and xylene, the wave-lengths being the spark lines Mg4481, Zn4912,24, Mg5173,83, Cd5338,78. It is found in every case that the differences in the time-lags of the Faraday effect behind the magnetic field are inversely proportional to the wave-lengths of light used. The extreme variations observed in these time-lag differences range from 0.3×10^{-9} sec. for the longer wave-lengths to 7.5×10^{-9} sec. for the shorter waves, depending upon the two liquids compared, the precision of an observation being 0.3×10^{-9} sec.

68. Relation of heat transmission to humidity in insulating materials. L. F. MILLER, University of Minnesota.—The hot and cold plate apparatus, with guard ring, taking twelve inch square samples was used, which seems best for preserving the moisture content acquired at the different humidities. Measurements were made at the same humidities to which the sample was exposed. To avoid short circuiting thermocouple due to wetting, enameled Advance (formerly Ideal) and copper wires were employed. Special apparatus was used to humidify the room and moisture content was measured by weighing. As checks, three different instruments measured the relative humidity, one

instrument being a continuous recorder. Materials investigated were: wood-pulp fibre, flax-fibre, cane-fibre and rag-paper felt, all approximately 1/2 inch thick. All thermocouples used were found to be reliable to 1/10°C. The temperature difference was not much over 10°C, which reduces the tendency of the moisture to move from hot side toward the cold side. Indication of results is that the heat transmission increases linearly as the moisture content. Up to 100 percent relative humidity there is an average increase in moisture content of about 15 percent by weight of dry sample weight and about a 15 percent increase in heat transmission for the four materials. At 100 percent relative humidity absorption is more rapid and moisture content much greater, with corresponding increase in thermal-conductivity.

69. Thermal expansion of graphite. PETER HIDNERT and W. T. SWEENEY, Bureau of Standards.—An investigation on the thermal expansion of longitudinal and transverse sections of artificial graphite (99.2 to 99.7 percent carbon) over various temperature ranges between room temperature and 600°C has recently been completed. The coefficients of expansion of graphite are low. For example, the coefficient of expansion of ordinary steel is about six times the coefficient of longitudinal sections of graphite and about four times the value for transverse sections between 20 and 100°C. The transverse samples expand considerably more than the longitudinal samples (approximately 45 percent). The coefficients of expansion increase with temperature. For both the longitudinal and transverse sections, the coefficients of expansion decrease slightly as the purity (carbon content) increases. The following table gives a resumé of average coefficients of expansion for various temperature ranges.

	Average Coefficient of Expansion ($\times 10^6$) *per Degree Centigrade*					
Section	20 to 100°C	20 to 200°C	20 to 300°C	20 to 400°C	20 to 500°C	20 to 600°C
Longitudinal	1.9	2.0	2.2	2.4	2.5	2.7
Transverse	2.9	3.0	3.2	3.5	3.6	3.7

70. Theory of the magnetic nature of gravity. CORNELIO L. SAGUI, Castelnuovo dei Sabbioni, Italy.—The only physical reality considered necessary is the electromagnetic field. A ray of light is considered as formed of a series of extremely small electrical resonators without ohmic resistance. In such a resonator a sine disturbance once started will go on without end. A transmitting medium for the energy is not considered necessary. The electromagnetic waves would consist of a sort of magnetic quanta moving to and fro. Matter would be built up similarly of electrical resonators, so that the gravitational force would be represented by the integral value of all the magnetic quanta of the elementary resonators moving to and fro about the body in a radial direction, at a distance which should be a function of the total number of resonators composing the body in question. Thus the gravitational field would not be infinite, but limited by the mass of the body itself. A ray of light going through a gravitational field of such a kind must modify its frequency within certain limits. A second modification of its frequency would result from the motion of the earth, in such a way that when the motion was in the same direction as that of the ray the frequency would become smaller.

71. Cosmic aspects of atmospheric electricity. LOUIS A. BAUER, Carnegie Institution of Washington.—There being at present no generally accepted theory to account for the origin and maintenance of the earth's negative electric charge, it is of peculiar interest to study the laws and modus operandi of the changes to which atmospheric electricity is subject during the day, year, and from year to year. These changes, which even on meteorologically-undisturbed days are on the order of the absolute values of the atmospheric elements themselves, show remarkable terrestrial and cosmical aspects; i.e., they are in general of the same character and sign at stations both in the northern and southern hemispheres. Recent world-wide observations give further confirmation

of these striking facts. A brief discussion is also given of the relation of the atmospheric-electric results to recent measurements of the ozone content of the atmosphere, of the sun's ultra-violet radiation, of radio-reception, and of solar activity.

72. Measurements of the variation of residual ionization in air with pressure at different altitudes. W. F. G. SWANN, Yale University.—Under the auspices of the Bartol Research Foundation, measurements of residual ionization were made, in an iron sphere, at Colorado Springs and at the summit of Pikes Peak, for pressures ranging from atmospheric up to 1000 lbs. per square inch. In one set of experiments the iron sphere one inch in thickness was shielded by about 2 inches of lead and in the other set it was unshielded. Corresponding observations were reproducible with an accuracy of about 2 percent. The mean apparent absorption coefficient α (the coefficient calculated for the case of a vertical radiation) was $5 \cdot 2 \times 10^{-4}$ per meter of air estimated at atmospheric pressure, and it was the same to within a few percent of its value from whatever corresponding parts of the pressure ionization curve it was calculated. The increase in ionization per atmosphere increase in pressure decreased with the pressure but became sensibly constant at the higher pressures. The absolute increase in ionization per cc per atmosphere increase in pressure at the highest pressures was 0.75 for the summit of Pikes Peak.

73. Radiometric measurements on the planet Mars, 1926. W. W. COBLENTZ and C. O. LAMPLAND, Bureau of Standards.—Measurements with vacuum thermocouples intercepting only 0.01 of the area of the planetary image confirm previous observations, showing: the southern (summer) hemisphere warmer than the northern hemisphere; the dark areas hotter than the adjacent bright areas; the forenoon side cooler than the afternoon side (exceptions; sunset clouds, or dark area on east limb irradiated an hour before sunrise). Temperature differences between the center of the disk and the limbs (and poles) appear smaller than previously observed; probably seasonal, which was a month after Martian summer solstice instead of a month before as obtained in 1924. Owing to clouds and the "limb light" of the Martian atmosphere, estimates of temperatures on east and west limbs are too low. Afternoon clouds seemed denser than morning clouds—not necessarily a general condition. The following tentative estimates of Martian surface temperatures are given; as viewed on the central meridian, the south polar region 10° to −10°C; south temperature zone 20° to 25°C (clouds—10°C); center of disk 20° to 30°C; north temperature zone 0° to 20°C; north polar region −25° to −40°C; east limb (after being irradiated for an hour) −20°C, no phase −25°C, clouded −35°C; west limb (terminator) 0°C, no phase −10°C, clouded −30°C.

74. On the effects of dust, smoke, and relative humidity upon the potential gradient and the positive and negative conductivities of the atmosphere. G. R. WAIT, Carnegie Institution of Washington.—A discussion is given of simultaneous observations of atmospheric electricity, dust-content, and relative humidity obtained at the Watheroo Magnetic Observatory, Western Australia.—The dust-content series (by Aitken's counter) during February to April, 1924, gives consistent results indicating that the potential gradient is approximately doubled for increase of dust-content from zero to 10,000 particles per cubic centimeter and thereafter a very slow increase with increased dust-content. Thus one is not justified in extrapolating, as has been done, values for dust-free air when the data are obtained only for high dust-contents. Both positive and negative conductivities decrease about half when the dust-content changes from zero to about 5,000 particles per cubic centimeter and decrease very slowly thereafter with increased dust-content. The ratio of positive to negative conductivity, as might be expected, increases with increasing dustiness. The more extensive simultaneous observations of the atmospheric-electric elements and relative humidity, using data taken only at times of low dust-content, show that these elements are similarly affected by an

increase in relative humidity, but to a lesser extent. The analysis shows that very few transformed large ions pass through the conductivity instruments without being recorded. The great importance of more observations of this kind in investigating the behavior of ions in air is pointed out.

75. Demonstration of an improved form of Rijke tube of high efficiency. A lecture experiment in acoustics. R. W. WOOD, Johns Hopkins University.—By increasing the number of gauzes, a tube was constructed which continued sounding for two minutes or longer.

76. The direct comparison of the loudness of pure tones. B. A. KINGSBURY, Bell Telephone Laboratories, Inc.—The intensities of 11 pure tones necessary to make them as loud as certain fixed levels of a 700 cycle test tone were judged by 22 observers, 11 men and 11 women. Frequencies from 60 to 4000 cycles were used and intensities from the threshold of audibility to levels somewhat louder than ordinary conversation. It was found that if the amplitudes of pure tones are increased in equal ratios the loudness of low frequency tones increases much more rapidly than that of high frequency tones although for frequencies above 700 cycles the rate is nearly uniform. As a loudness unit the least perceptible increment of loudness of a 1000 cycle tone was employed. In absolute magnitude this varies from level to level, but in the ordinary range of loudness it becomes constant. The variability of the data from which the averages were computed was separated into a factor expressing dissimilarity of ears and another expressing errors of observers' judgment. There was no level at which the variances were a minimum. Dissimilarity of ears causes more variation than errors of observers' judgment.

77. Physical and biological effects of high-frequency sound waves of great intensity. R. W. WOOD, Johns Hopkins University, and ALFRED L. LOOMIS, Tuxedo, N. Y.—This paper describes effects observed with sound-waves of 300,000 vibrations per second, obtained with a piezoelectric quartz plate driven by an electrical oscillator of 2 kilowatts output at 50,000 volts; thermic effects; elevation of the free surface of the liquid by the pressure of the waves; atomization of the surface with waves of great intensity; destruction of the red blood corpuscles in a living animal and other biological effects.

AUTHOR INDEX

Allis, W. P. and **H. Mueller**—No. 35.
Allison, Fred—No. 67.

Barrett, C. S. and **J. A. Bearden**—No. 33.
Bauer, Louis A.—No. 71.
Bayley, P. L.—No. 6.
Beams, J. W. and **Earnest O. Lawrence**—No. 20.
Beams, J. W.—See **Lawrence.**
Bearden, J. A.—see **Barrett.**
Becker, J. A.—No. 44.
Begeman, Hilda—see **McDowell.**
Bennett, R. D.—No. 43.
Birge, R. T. and **J. J. Hopfield**—No. 8.
Black, J. G.—see **Duffendack.**
Boord, Cecil E.—see **Smith.**
Bourgin, David G.—No. 59.
Breit, G.—No. 34.

Coblentz, W. W. and **C. W. Hughes**—No. 48.
Coblentz, W. W. and **C. O. Lampland**—No. 28.

del Rosario, C.—No. 31.
Duffendack, O. S. and **J. G. Black**—No. 24.

Ellis, Joseph W.—No. 19.
Erikson, Henry A.—No. 63.

Frank, N. H.—No. 50.
Franklin, Wm. S.—No. 39.
Frayne, John G. and **C. W. Jarvis**—No. 22.
Friauf, James B.—No. 8.

Gartlein, C. W.—No. 21.
Gibbs, R. C. and **H. E. White**—No. 28.

Gibbs, R. C.—see **White.**
Gray, J. A. and **B. W. Sargent**—No. 1.

Ham, W. R.—No. 45.
Harrington, E. A.—No. 7.
Harrington, G. F. and **A. M. Opsahl**—No. 46.
Harrison, J. R.—No. 51.
Henderson, Jos. E.—No. 61.
Hidnert, Peter and **W. T. Sweeney**—No. 69.
Hopfield, J. J.—No. 17.
————see **Birge.**
Horovitz, Karl—No. 4.
Hughes, A. L. and **A. M. Skellett**—No. 47.
Hughes, C. W.—see **Coblentz.**
Hulburt, E. O.—No 49.
Hutchisson, Elmer—No. 33.

Ives, Herbert E.—No. 42.

Jarvis, C. W.—see **Frayne.**
Johnson, J. B.—No. 57.

Karapetoff, Vladimir—No. 56.
King, Arthur S.—No. 27.
Kingsbury, B. A.—No. 76.
Kleeman, Richard D.—Nos. 60, 62.

Lampland, C. O.—see **Coblentz.**
Lawrence, Ernest O. and **J. W. Beams**—No. 36.
Lawrence, Ernest O.—see **Beams.**
Lilienfeld, J. E. and **C. H. Thomas**—No. 54.
Loomis, F. W.—No. 15.
Lubovich, Vladimir P.—No. 16.

McDowell, Louise S. and **Hilda Begeman**—No. 55.
Meggers, W. F. and **F. M. Walters**—No. 26.
Miller, L. F.—No. 68.
Mohler, F. L.—No. 13.
Mueller, H.—see **Allis.**

Nathanson, J. B.—No. 64.
Nusbaum, C.—No. 66.

Opsahl, A. M.—see **Harrington, G. F.**

Pease, C. S.—see **Smith.**
Piersol, Robert J.—No. 40.
Purks, J. H. and **C. M. Slack**—No. 3.

Richtmyer, F. K. and **L. S. Taylor**—No. 9.
Rudy, Richard—No. 30.
Rusk, Rogers D.—No. 11.

Sagui, Cornelio L.—No. 70.
Sargent, B. W.—see **Gray.**
Sawyer, R. A. and **F. R. Smith**—No. 23.
Schneider, W. A.—No. 41.
Skellett, A. M.—see **Hughes, A. L.**
Slack, C. M.—see **Purks.**
Smith, Alpheus W., Cecil E. Boord and **C. S. Pease**—No. 14.
Smith, F. R.—see **Sawyer.**
Sommer, L. A.—No. 25.
Stilwell, G. R.—see **Ives.**
Stuhlman, Otto—No. 10.
Swann, W. F. G.—No. 72.
Sweeney, W. T.—see **Hidnert.**

Taylor, L. S.—see **Richtmyer.**
Taylor, Paul B.—No. 61.
Terry, Earle M.—No. 52.
Thomas, C. H.—see **Lilienfeld.**
Tschudi, E. W.—No. 12.
Tykocinski-Tykociner, J.—No. 53.

Wait, G. R.—No. 74.
Walters, F. M. Jr.—see **Meggers, W. F.**
Waterman, A. T.—No. 58.
Weigle, J. J.—No. 37.
White, H. E. and **R. C. Gibbs**—No. 29.
White, H. E.—see **Gibbs.**
Wilkins, T. R.—No. 2.
Williams, S. R.—No. 65.
Witmer, Enos E.—No. 38.
Wood, R. W.—Nos. 75, 77.